THE SIMULATION OF FIXED-BED ION EXCHANGE COLUMNS

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SUMMARY

The equations for the fixed-bed ion exchange process have been rigorously solved to give breakthrough curves using analog, digital and hybrid computers.

The models developed for the ion exchange column process are general enough to include:-

- Linear and non-linear equilibrium
- Constant or variable separation factor
- Mass transfer resistance in either the solution or the resin phase, or both
- Axial dispersion
- General initial conditions for column presaturation
- Arbitrary boundary conditions for partial or complete breakthrough curves.

Results indicate that simple rate relations are adequate to express column behaviour for most requirements. In particular, the Thomas model as developed by Hiester and Vermeulen is easy to use and sufficiently accurate for normal applications.

A comparison of computed results with experimental data has shown that the ion exchange column process can be accurately simulated. However, this required the use of a variable separation factor for some systems.

CHAPTER 1

INTRODUCTION

Ion exchange is one of many adsorption processes in which a solute is preferentially removed from a fluid and held, generally reversibly, in a solid phase.

However, ion exchange differs from the other adsorption processes, which are selective surface condensations, in that:-

- the exchanging species is an ion
- the adsorbing ion stoichiometrically displaces another from the solid phase
- the adsorbed ion is held by ionic attraction within the solid.

Selectivity is by ionic change complicated by size and concentration.

Many materials have been used as the solid phase in ion exchange. Helfferich (1962) reports that Moses used a tree for a conventional water-softening application. Adams and Holmes (1935) discovered that crushed gramophone records had exchange properties, leading to the synthesis of polymeric organic ion exchange resins which are now used for nearly all laboratory and industrial applications.

Modern synthetic resins can be considered as a polymeric matrix containing fixed charges, to which ions are bonded by electrical attraction, but not so strongly that they cannot be replaced by other ions, with greater selectivity or availability.

1-1. The Fixed-bed Ion Exchange Process

The ion exchange process may be operated as:

- a stirred reactor, with the resin agitated in the solution (batch operation)
- with the resin stationary in a column, with the solution percolating through the interstices of the particles (fixed bed operation).
- with the resin moving in the column counter current to the percolating solution (moving bed operation).

Batch operation suffers from providing only one equilibrium stage, but may be used in cascade. It is sometimes used when mass transfer rates are low and when small particles or suspended solids would cause

high column pressure drop. Moving-bed operation is continuous and countercurrent, analogous to gas absorption or liquid extraction. The problems of solids handling and resin degradation are only slowly being solved.

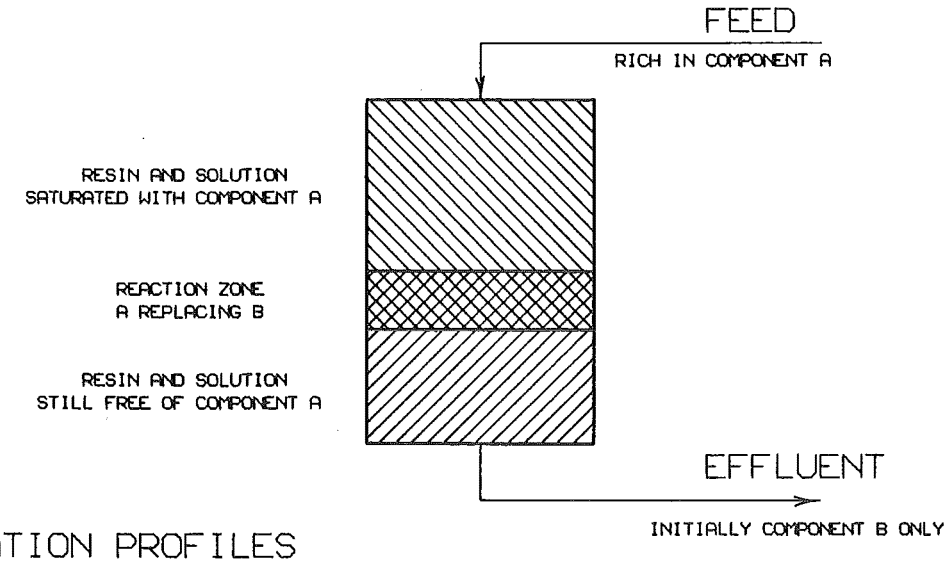
The fixed bed ion exchange column is the common method of operation. The equipment is simple and reliable, easily automated and will operate with low pressure drop over a wide range of flow rates.

The feed solution containing the ion to be removed is fed to the top of a vessel containing the bed of resin particles. As the ion, say A, flows down the column, it comes into contact with resin containing the ion to be replaced, B. Either because of selectivity or concentration effects, A will be adsorbed, to displace B from the resin into the solution and eventually from the column into the product stream. The exchange process occurs in a section of the bed, the reaction zone. As more feed solution is passed through the column, more resin will be in the A form and the feed must pass further down the column to reach the fresh resin in the B form. The reaction zone thus moves down the column, until the bottom of the column is reached when the effluent will be no longer free of ion A, and a substantial portion of the resin converted to the A form. This history is shown in Fig. 1-1 with column concentration profiles and the breakthrough curve.

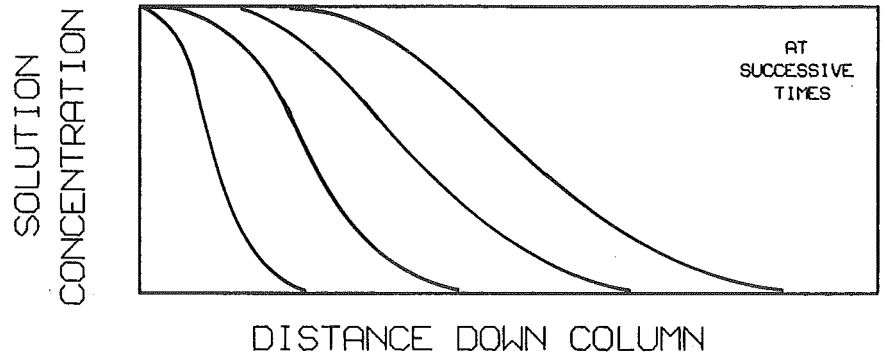
Before the column can be reused it must be returned (regenerated) to the B form with a suitable regenerant solution containing B.

The fixed-bed ion exchange process will produce substantially pure product, since the effluent has been in contact with regenerated resin until breakthrough. In the absence of resin poisons, the resin life is long and losses are small. However, the fixed-bed ion exchange process has disadvantages:

- it is a batch operation and may not integrate well with typically continuous chemical processing although adequate storage and simple scheduling can minimise this problem
- the capacity of the resin is rather small (typically several milli-equivalents per gram) and operating costs (principally for regeneration and resin inventory and replacement) appear



CONCENTRATION PROFILES



BREAKTHROUGH CURVES

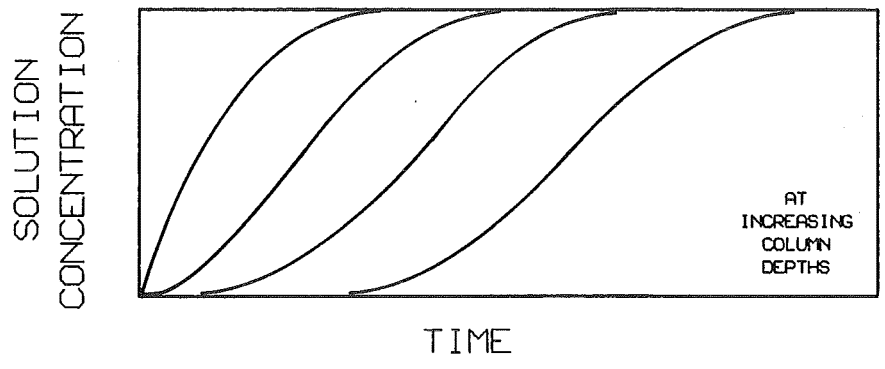


FIGURE 1-1. ION EXCHANGE COLUMN CONCENTRATIONS.

large when expressed per unit of solute removed. However, this cost is often uniquely low if expressed per unit of feed solution treated. The process is particularly suitable for removing trace components as the bulk stream is unaltered, only the minor component being transferred.

- the resin is not fully utilised at any one time in a fixed bed, only that portion in the exchange zone is being used, perhaps less than 20% of the resin.

Design of a fixed-bed ion exchange process begins with choice of the resin for favourable selectivity (but not so favourable as to inhibit regeneration), adequate capacity, and satisfactory physical and chemical properties for long life. The resin size is restricted to the manufacturer's range, and pressure drop is balanced against mass transfer rates. Considerable flexibility remains in the number of beds, their arrangement in series or parallel, the operating schedule, the bed diameter and height, the interstitial velocity, the regenerant solution concentration and the degree of regeneration. Breakthrough curves are required for all these circumstances, both complete and partial. Methods of predicting breakthrough behaviour are essential, both for design and for the interpretation and correlation of available experimental data.

1-2. Simulating the Fixed-Bed Ion Exchange Process.

The purpose of this thesis has been to develop rigorous methods of simulating the performance of fixed-bed ion exchange columns in order:-

(a) To compare their behaviour with experimental data

(b) To investigate the significance of various assumptions and adsorption mechanisms

(c) To judge the effectiveness of available approximate breakthrough curve equations

(d) To establish a general presentation of ion exchange column results which could thereafter be used without recourse to further extensive computation.

Fixed-bed operation is difficult to describe mathematically and consequently to interpret and to scale-up. A moving-bed process is

straightforward as it is a steady-state mass-transfer column. A batch system, while not steady state, contains one fewer independent variable (distance down the bed).

Mathematical models of the fixed bed process are constructed in terms of equilibrium relations, material balances and diffusion and kinetic expressions which relate solution and resin concentrations to the operating parameters and time, subject to the geometry of the unit. These models do not aspire to be a fundamental expression of ion exchange column behaviour, but only to describe it in terms of measurable and correlatable quantities. The resultant equations are still sufficiently complex to render an analytical solution unlikely, and to require numerical or analogue solution. Such a simulation should be simple to use and sufficiently fast to make its routine use feasible, both for predicting behaviour for design decisions or for analysing experimental results.

Both the model and the method of solving the equations must be verified - the model against experimental results and the method against other methods and physical consistancy.

Some of the basic assumptions used in the development of this thesis are summarised below. Other particular assumptions are discussed as they arise.

(a) The column is isothermal. Since the ion exchange reaction is physical rather than chemical with consequent small heat of reaction, and since the fluid has a high heat capacity, temperature changes will be negligible.

(b) The bulk concentration in the fluid (or at any point in the particle) can be expressed in terms of one variable.

This limits the direct application of this work to single solute adsorption or to binary ion exchange. In general, extension to multicomponent operation is straightforward, requiring only that the equations be repeated and solved for each component, and that an adequate expression for multicomponent equilibrium behaviour be available.

(c) The feed rate to the column is constant

(d) The velocity profile across the column is uniform (plug-flow)

(e) The concentrations across the particle-solution interface are in equilibrium

(f) The ion exchange is of the strong acid-strong base type, so that the kinetics of the ion exchange reaction are not significant.

(g) The resin particle is spherical and a homogeneous, gel-like, pore-free macro molecule.

(h) The swelling properties do not affect the overall properties of the column. Since the bed-length parameter is normalised to a dimensionless number of transfer units reflecting the exchange capacity of the column, rather than its physical length, swelling properties can be ignored unless they are so gross as to distort the flow geometry.

Other assumptions common to the analysis of fixed bed operations have not been required. The basic model includes non-linear equilibrium and mass transfer resistance in both the solution and the particle phases. Axial dispersion, arbitrary equilibrium isotherms, uniform or non-uniform particle presaturation of the bed, an arbitrary feed concentration history and partial regeneration or exhaustion can be investigated.

While the techniques developed here are directed principally towards the ion exchange process, they can also be applied with minor modification to other fixed bed adsorption processes:

- adsorption on particulate solids, active carbon, molecular sieves
- adsorption drying of gases on silica gel, activated alumina.
- gas and liquid chromatography
- heat regenerators
- leaching

or with greater modification to

- fixed bed reactors
- batch distillation in packed columns.

CHAPTER 2

THE FIXED-BED ION EXCHANGE EQUATIONS

The equations which describe the fixed-bed ion exchange process are derived from:

- an equilibrium isotherm which relates the resin and solution concentrations at the interface and which is a property of the particular resin-solution system
- the rate equations arising from mass transfer limitations within the solution or the resin - a property of the resin, the system geometry and the method of operation
- the mass balance equations, dependent on the system geometry
- the initial and boundary conditions which reflect the method of operating the column.

A mathematical model of the process is constructed when the appropriate equations are combined into a totality which is sufficient to describe the process. Various models result as physical behaviour is expressed in different ways or as mechanisms are modified or ignored.

Prediction of fixed-bed ion exchange performance requires that the mathematical model be solved. Mathematical difficulties with the solution have frequently lead to a modification of the model to make the equations more tractable. A compromise is required between rigour and generality on the one hand and ease of solution and use on the other. The availability of computers - both digital and analog - has altered the balance of this compromise.

2-1. The Equilibrium Relation

The equilibrium between free and bound ions in an ion exchange resin bead and the surrounding solution is represented by a simple mass-action relation based on the replacement reaction

$$A^+ + BR \rightleftharpoons B^+ + AR$$

where A,B are the replacing counter ions and R denotes the resin. The separation factor, K, is defined:-

$$K = \frac{q_A \quad c_B}{q_B \quad c_A} \tag{2-1}$$

where c and q are the phase concentrations in the solution and resin, expressed in equivalents per litre of solution, or equivalents per volume of packed bed in the case of the resin. The separation factor is analogous to relative volatility in distillation practice.

The separation factor is normally taken as a constant (Vermeulen, 1958, page 160) for specified resin, feed concentration, species exchanging, pressure and temperature. Other authors (Hiester and Vermeulen, 1952; Reichenberg, 1966; Diamond and Whitney, 1966; Helfferich, 1962, Chapter 5) have discussed the variation in separation factors due to unequal valence of exchanging ions and to effects of solution concentration and activity.

Unequal valence can be accounted for by a modified approximate selectivity. Concentration effects require more complex expressions including activity terms. Reichenberg has examples of equilibrium reversing from favourable ($K > 1$) to unfavourable ($K < 1$) with concentration change - behaviour analogous to an azeotrope. For two ions of equal valence, the changes in activity in each may be small or equivalent, particularly for dilute solutions, allowing the separation factor to be assumed constant.

However, this thesis has not made this assumption, although each of the various models developed have initially used a constant separation factor. Arbitrary equilibrium expressions can be introduced into the computer models without fundamental modification to the method of solution since the change is to an algebraic rather than a differential equation. The computed results themselves, however, may be significantly different. The validity or otherwise of the assumption of a constant separation factor for column operation must be judged against experimental breakthrough curves.

2-2. Normalised Concentration Variables

Breakthrough curves and column behaviour can be generalised if concentrations are expressed as a ratio of the maximum concentration in the particular phase.

For the liquid phase in a column, the maximum concentration is the concentration of the feed stream. Since this is typically constant, say C_o equivalents/litre, the fluid concentration may be expressed as the solution concentration ratio, x, where

$$x = \frac{c}{C_o} .$$

The maximum concentration in the resin phase will correspond to the resin capacity - the number of equivalents of counter-ions in a specified quantity of resin. Many capacity bases have been used (Helfferick, 1962, page 73; Hiester et al., 1963) even ignoring the problems of resin wetness. The mathematical expression of column behaviour is more simple if the resin capacity, Q, is expressed as equivalents per volume of packed bed. This is not a fundamental quantity, but will depend on the resin form and its bulk density.

The resin concentration ratio is defined

$$y = \frac{q}{Q} .$$

The equilibrium isotherm can be written

$$K = \frac{y_A \quad x_B}{y_B \quad x_A} \qquad (2\text{-}2)$$

Since the exchanging species are charged ions and the resin and solution must remain electrically neutral (the electroneutrality condition) the total ionic concentration in each phase must be constant. In particular, binary exchange can be expressed in terms of the concentration of only one component since the concentration of the other is available from the relations

$$\begin{aligned} c_A + c_B &= C_o \qquad & x_B &= 1 - x_A \\ & \text{or} & & \qquad (2\text{-}3) \\ q_A + q_B &= Q \qquad & y_B &= 1 - y_A \end{aligned}$$

The equilibrium relation (Equation 2-1) becomes

$$\frac{y}{1-y} = \frac{K\,x}{1-x} \qquad (2-4)$$

if x and y are in equilibrium.

2-3. Mass Transfer Limitations

Ion exchange at some level in a column may be occurring at a sufficient rate that the movement of counter ions to and from the interface may be hindered by diffusional resistance in either or both phases. The bulk concentrations in each phase may not then be in equilibrium.

The processes of diffusion of one ion into the resin and the other to the solution are coupled by the electro-neutrality condition. The ion diffusing at the higher rate will cause an electric potential gradient to retard the fast ion and accelerate the slow ion.

Figure 2-1 shows the concentration gradients assumed to exist in the resin bead. The resistance to mass transfer may lie significantly in both phases as shown, or predominantly or completely in one.

Other diffusion and reaction possibilities exist with weak acid-weak base resins, with reactive systems (ion exchange followed by neutralisation or complex ion formation) and with non-homogeneous, macroporous resins. These have not been further considered here (Helfferich; 1966, Chapter 2).

2-3-1. Particle Diffusion

For diffusion through a homogeneous, water-permeable, non-porous, spherical solid, concentration change is expressed by Fick's laws (Helfferich, 1962; 1966)

$$\frac{dq}{dt} = D\left(\frac{\partial^2 q}{\partial r^2} + \frac{2}{r}\frac{\partial q}{\partial r}\right) \qquad (2-5)$$

D the diffusivity (L^2T^{-1})

q resin concentration

r radial distance (L), assuming spherical symmetry

t time (T)

Fick postulated that the diffusivity was constant. Ion exchange is more complicated because both counter-ions (the replaced and replacing) are diffusing in opposing directions with different diffusivities, say

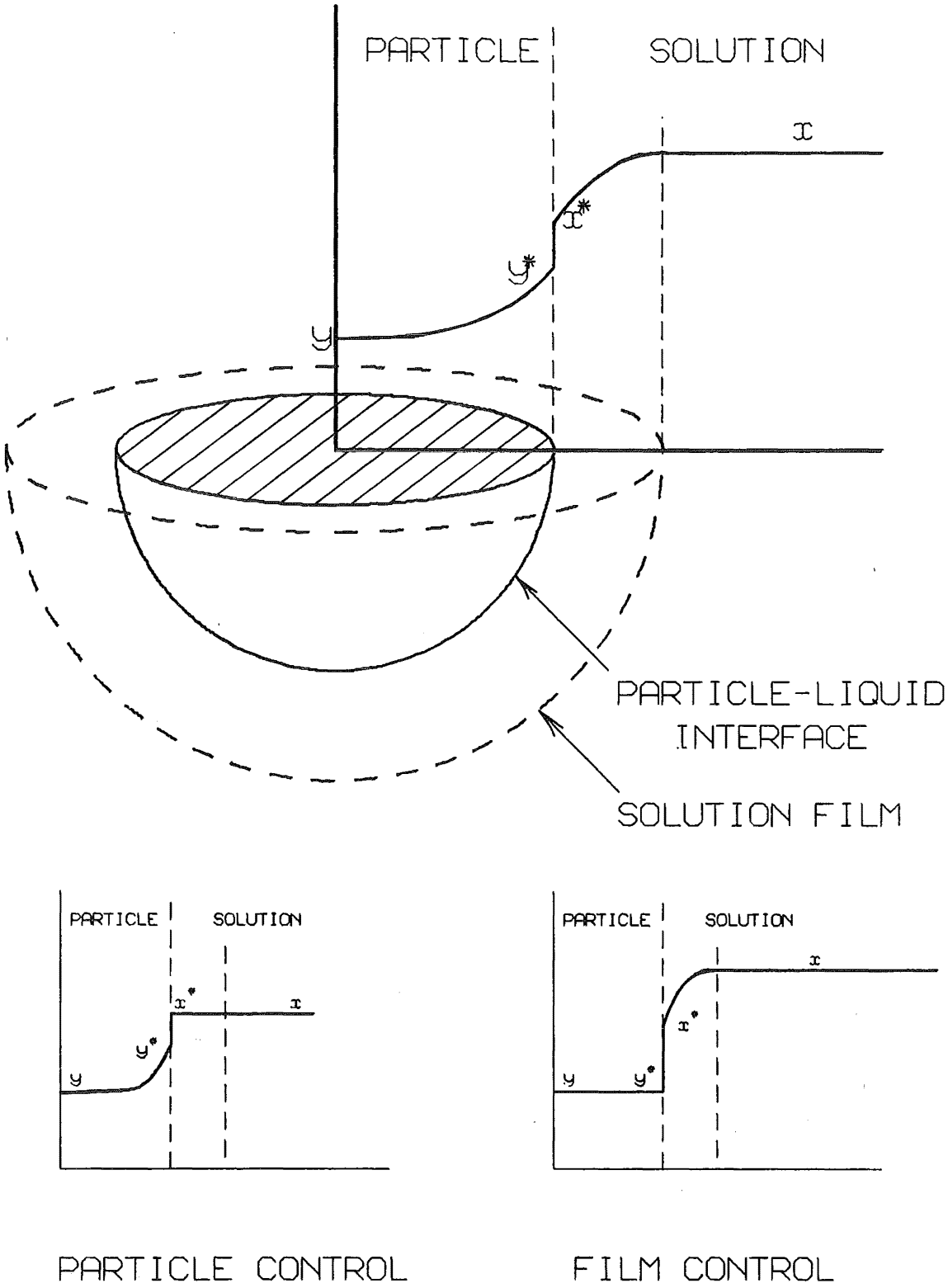


FIGURE 2-1. PARTICLE AND SOLUTION CONCENTRATION GRADIENTS.

D_A and D_B, but linked by the electro-neutrality condition.

The Nernst-Planck equation (Helfferich, 1962, page 268) can be applied to each counter-ion, to include both the diffusion flux and transference resulting from the resultant potential gradient. These equations can be solved under the electro-neutrality condition and the relaxation of the electric field assuming that the effects of pressure gradients, activity coefficients, the presence of co-ions and variations in self-diffusivities can be ignored. The result is an equation of the same form as Eqn 2-5, but the diffusivity is not constant, being replaced by the concentration-dependent interdiffusivity,

$$D_{AB} = \frac{D_A D_B (e_A^2 q_A + e_B^2 q_B)}{e_A^2 q_A D_A + e_B^2 q_B D_B} \qquad (2\text{-}6)$$

where D_A, D_B are self-diffusivities (L^2T^{-1})

e_A, e_B are valences of A,B.

The Nernst-Planck form indicates the inter-diffusivity is not constant during exchange unless

$$e_A = e_B$$

and $$D_A = D_B$$

which is strictly true only for isotopic exchange. Notwithstanding, the fickian form (constant interdiffusivity) is commonly used for ion exchange (Rosen, 1952, 1954; Vermeulen, 1958; Hiester, 1963).

Kelly (1966) has reviewed the experimental verification of the Nernst-Planck and fickian equations, and has concluded that the integrated form of either can describe experimental data satisfactorily, provided the self-diffusivities or the interdiffusivity is chosen to give the best fit and not taken from independent a priori measurement or theory. Helfferich (1966, page 79) strongly supports the Nernst-Planck form.

Results obtained for a single particle of Dowex 50W-X8 placed in a bed of similar sized glass spheres using sensitive radiochemical tracer techniques for Ca^{++}/Na^{+} (Morig and Rao, 1965; Kuo and David, 1963; Rao and David, 1964) could be expressed by a constant inter-diffusivity. On the other hand, Turner et al. (1966) have shown that for H^{+}/Na^{+} exchange on Zeo-Karb 225 in batch operation for small solution and resin concentration changes, the inter-diffusivity was not constant,

being closely given by

$$D_{AB} = \frac{D_A}{1 + y(\frac{D_A}{D_B} - 1)}$$

modified for univalent-univalent binary exchange with D_H, D_{Na} equal to 5.7, 1.2 $\times 10^{-6}$ cm^2/sec respectively.

As a further simplification, a linear rate equation

$$\frac{dq}{dt} = k_p(q^*-q) \text{ or } \frac{dy}{dt} = k_p(y^*-y) \qquad (2\text{-}7)$$

is often used, where:-

k_p Mass transfer coefficient (T^{-1}), given by $\frac{60\ D_p}{d_p^2}$ (Glueckauf and Coates, 1947)

D_p Inter-diffusivity ($\frac{L^2}{T}$)

d_p Particle diameter (L)

This simplification implies that the average resin concentration $\bar{y}$ is equal to the bulk value y, i.e.

$$\bar{y} = y \qquad (2\text{-}7a)$$

Only the linear and fickian rate equations have been implemented in this thesis although the required extension to the Nernst-Planck equation is simple.

When ionic self-diffusivities can be reliably predicted in resins, there may then be a need for this further extension. Such prediction is made difficult by:

- variability in the resin matrix, the framework through which diffusion must occur
- variation in the resin between and within batches
- interaction between the counter-ions and other fixed groups
- the entry of co-ions into the resin, notwithstanding Donavan exclusion
- the non-homogeneous nature of the resin.

One of the conclusions of this work is that column behaviour is not strongly dependent on the rate expression, at least for linear, fickian or reaction kinetic expressions. For practical purposes of column operation the lesser conflict between fickian and Nernst-Planck

forms may be immaterial.

2-3-2. Film Diffusion

The solution phase mass transfer rate is often expressed by a linear driving force

$$\frac{dy}{dt} = k_f \quad (x-x^*) \qquad (2-8)$$

where k_f is a film mass transfer coefficient (T^{-1}).

Correlations suggested for k_f have been of the form

$$j_d = a(N_{Re})^b$$

where j_d is a mass transfer j factor and N_{Re} is a Reynold's number (Vanichseni, 1970). Vermeulen's correlation for ion exchange (Hiester et al., 1956) is a typical example:-

$$j_d = 0.38 \ (N_{Re})^{-0.51}$$

where

$$j_d = \frac{k_f}{v}\left(\frac{\mu}{\rho D_f}\right)^{\frac{1}{2}}$$

$$N_{Re} = \frac{d_p v \rho}{6(1-\varepsilon)\mu}$$

D_f solution diffusivity (L^2T^{-1})

ε voidage

μ, ρ solution viscosity ($\frac{M}{LT}$), and density ($\frac{M}{L^3}$).

This linear expression ignores the coupled nature of ionic diffusion, and as for particle diffusion, the Nernst-Planck equation has been applied to the film mass transfer resistance (Dranoff, 1964; Lupa, 1967; Turner, 1968 , 1970; Kataoka, 1968).

However, for the available results, Helfferich (1966, page 85) suggests that either the linear approximation or the Nernst-Planck equation are equally satisfactory. Only the linear form is used in the models in this work.

2-3-3 Pore Diffusion.

If fissures exist in the resin, then mass transfer can be enhanced by pore diffusion. Conventional strong-acid/strong-base ion exchange resins are homogeneous and non-porous, and pore diffusion will not be further considered. This would not be justified with many industrial

surface adsorbents.

2-4. The Solution Mass Balance

A mass balance taken over a cross-sectional element of an isothermal fixed-bed for an element of time equates the solute entering the element by mechanical transport and molecular diffusion in the mobile phase with:

- solute leaving the element by these mechanisms
- change in the solute held in the element, both in the mobile and stationary phases.

For each component (Rachinskii, 1965)

$$\frac{\partial c_i}{\partial t} + \frac{1}{\varepsilon}\frac{\partial \bar{q}_i}{\partial t} + \mathrm{div}(c_i \underline{u}) = D_i \Delta c_i \qquad (2\text{-}9)$$

where:-

c_i, q_i are the concentrations in the solution, resin respectively of the species i

D_i is the axial diffusivity for this component (L^2T^{-1})

ε is the column voidage

u is the interstitial velocity (LT^{-1})

If the mobile phase is incompressible, if its change in density with composition is negligible, if motion of the fluid is significant only in the axial direction of the bed (the one dimensional problem) and the velocity of the fluid is constant, then Eqn 2-8 simplifies to

$$\frac{\partial c_i}{\partial t} + \frac{1}{\varepsilon}\frac{\partial \bar{q}_i}{\partial t} + \frac{v}{\varepsilon}\frac{\partial c_i}{\partial z} = E_A \frac{\partial^2 c_i}{\partial z^2} \qquad (2\text{-}10)$$

replacing the interstitial velocity u by the superficial velocity v and writing the equation for binary exchange in terms of one component.

For most ion exchange applications molecular diffusion and other axial effects included in E_A are negligible (Vermeulen, 1952) and hence:-

$$\frac{\partial x}{\partial t} + \frac{Q}{\varepsilon C_o}\frac{\partial \bar{y}}{\partial t} + \frac{v}{\varepsilon}\frac{\partial x}{\partial z} = 0 \qquad (2\text{-}11)$$

2-5. The Particle Mass Balance

The solution mass balance uses the average particle concentration, $\bar{q}$. If a particle-side rate expression is used which requires the concentration, q, at some point within the resin taken as a function of the radial distance only (spherical symmetry is assumed), as in equations 2-4, 2-5 and 2-6, then the average particle concentration is

$$\bar{q} = \frac{24}{d_p^3} \int_0^{d_p/2} r^2 \, q \, dr \qquad (2\text{-}12)$$

A differential form of this expression can be obtained by equating the rate of diffusion from the surface into the particle with the change in $\bar{q}$:-

$$D_p \frac{dq}{dr}\bigg|_{r = d_p/2} \cdot \pi d_p^2 \cdot \rho = \frac{d\bar{q}}{dt} \cdot \frac{\pi}{6} d_p^3 \cdot \rho$$

and

$$\frac{d\bar{q}}{dt} = \frac{6D_p}{d_p} \cdot \frac{dq}{dr}\bigg|_{r = d_p/2} \qquad (2\text{-}13)$$

If on the other hand, the rate expression uses the bulk value (either the linear form, eqn 2-7, or the quadratic driving force, eqn 3-13), this corresponds to the average value since a flat concentration gradient is implied within the particle.

2-6. Boundary and Initial Conditions

The initial conditions are provided by the condition of the solution and resin in the column at the start of the exchange operation. For breakthrough curve calculation, the column is typically assumed to be in the completely regenerated form.

$$y = 0 \text{ at } t = 0, \; z > 0, \; 0 < r < d_p/2. \qquad (2\text{-}14)$$

The boundary conditions result from the method of operating the column, and are defined by the concentration history of the feed solution to the column. For complete exhaustion

$$x = 1.0 \quad \text{at } z = 0, \quad t > 0,$$

and for complete regeneration, x = 0.0 for the same conditions.

For partial saturation (partial exhaustion followed by regeneration)

$$x = 1.0 \quad \text{at } z = 0, \quad 0 < t < t^* \qquad (2\text{-}15)$$

$$x = 0.0 \quad \text{at } z = 0, \quad t \geq t^*$$

where t^* is the time at which the input concentration falls from the feed to the regenerant value.

Similar conditions apply to other adsorption processes, even pulse or elution chromatography, where t^* may tend to zero.

If longitudinal effects are not negligible (chapter 9) then the boundary condition must be modified to account for the reduction of the solution concentration at $z = 0$ (Danckwerts, 1953; Pearson, 1959; Bastion and Lapidus, 1956).

Figure 2-2 shows the bulk flows and the diffusional flux around the top element of the bed. A mass balance about this element gives

$$Fx_oC_o = FxC_o - \varepsilon A E_A \frac{\partial x}{\partial z} C_o$$

and the boundary condition is

$$x = x_o + \frac{\varepsilon E_A}{v} \frac{\partial x}{\partial z} \quad \text{at } z = 0, \; t \geq 0. \qquad (2\text{-}16)$$

2-7. The Normalisation of the Ion Exchange Equations.

A standard change of variables can be made to render the independent variables t,z,r dimensionless and to group parameters in significant dimensionless groups for greater generality.

The usual transformations are (ignoring axial dispersion):-

$$R = \frac{2r}{d_p} \qquad (2\text{-}17)$$

$$N_p = \frac{Q}{C_o} \frac{k_p z}{v} \quad \text{or} \quad N_f = \frac{Q}{C_o} \frac{k_f z}{v} \qquad (2\text{-}18a, 2\text{-}18b)$$

$$Z = \frac{C_o v}{Qz} \left(t - \frac{\varepsilon z}{v}\right) = \frac{T_p}{N_p} \text{ or } \frac{T_F}{N_F} \qquad (2\text{-}19)$$

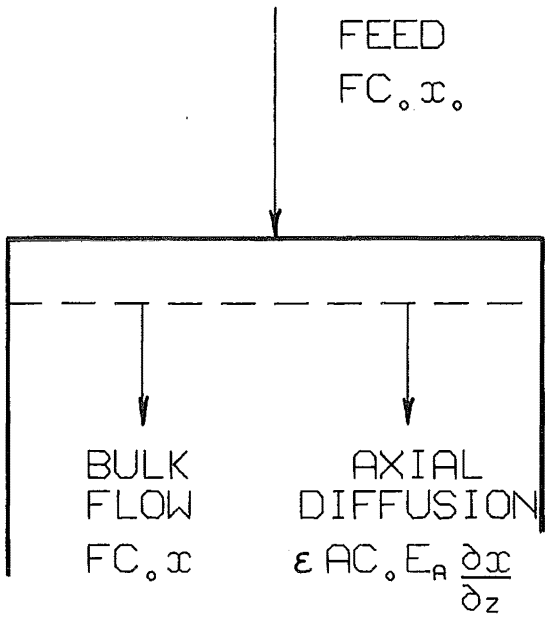
$$\xi = \frac{N'_p}{N'_{p\xi}} \qquad (2\text{-}20)$$

where:-

N_f, N_p Bed depth variables, based on the film or particle phase. Measured in numbers of transfer units.

N'_f, N'_p Total number of transfer units on the film, particle side respectively in the column.

Z Throughput ratio



A	SUPERFICIAL COLUMN AREA
C_o	TOTAL CONCENTRATION IN SOLUTION
E_A	EFFECTIVE AXIAL DIFFUSIVITY
F	FLOW RATE TO COLUMN
x_o	FEED CONCENTRATION RATIO
x	CONCENTRATION RATIO AT TOP OF BED
ε	VOIDAGE
z	BED DEPTH

FIGURE 2-2. FINITE BED BOUNDARY CONDITION FOR SIGNIFICANT AXIAL DISPERSION

T_f, T_p The characteristic time, based on the number of film, particle transfer units respectively.

ξ The mechanism parameter.

The model to be developed, and its solutions, should be as general as possible. It must allow mixed diffusion ($0 < \xi < \infty$) as well as particle diffusion control ($\xi = 0$) or film control ($\xi = \infty$). Computations are most easily organized, and results best expressed, in terms of the phase offering the greater resistance to mass transfer, i.e. the side with the smaller number of transfer units in the column. This implies two sets of equations - one for use with particle control, $N'_p < N'_f$ (particle phase basis) and the other for film control $N'_f < N'_p$ (solution phase basis).

However, Appendix 2A shows that the equations which will be needed later can be reduced to one set applying for all values of ξ, if expressed in terms of N and T, both defined in terms of the controlling phase

$\xi < 1$	$\xi > 1$
$N = N_p$	$N = N_f$
$N' = N'_p$	$N' = N'_f$
$T = T_p$	$T = T_f$
Particle Control	Film Control

The equations are written:-

Equilibrium

$$\frac{y^*}{1 - y^*} = K \frac{x^*}{1 - x^*} \tag{2-21}$$

Mass balances

$$\frac{\partial x}{\partial N} + \frac{\partial \bar{y}}{\partial T} = 0 \tag{2-22}$$

$$\bar{y} = 3 \int_0^1 y \, R^2 dR \tag{2-23a}$$

$$\frac{\partial \bar{y}}{\partial T} = \frac{\sigma}{5} \left. \frac{\partial y}{\partial R} \right|_{R = 1} \tag{2-23b}$$

Rate Equations

$$\frac{\partial \bar{y}}{\partial T} = \rho (x - x^*) \tag{2-24}$$

$$\frac{\partial \bar{y}}{\partial T} = \frac{\sigma}{15} \left(\frac{\partial^2 y}{\partial R^2} + \frac{2}{R} \frac{\partial y}{\partial R} \right) \tag{2-25a}$$

$$\frac{\partial \bar{y}}{\partial T} = \sigma (y^* - y) \tag{2-25b}$$

The values of ρ and σ depend on the mechanism parameter.

Basis	ξ	N	T	ρ	σ
Particle-phase $N'_p \ll N'_f$	$\xi \ll 1$	N_p	T_p	$\frac{1}{\xi}$	1.0
Solution-phase $N'_f < N'_p$	$\xi > 1$	N_f	T_f	1.0	ξ

TABLE 2-1. Values of ρ and σ for particle or film control. Both ρ and σ take values not less than 1.0.

2-8. The Overall Mass Balance

A useful relation results from an overall solute mass balance around a fixed bed. Solute added to the column is either adsorbed and retained in the column or not adsorbed and leaves in the effluent.

Figure 2-3 briefly derives the relation for a partly saturated bed. The total solute adsorbed in the column up to the time the effluent volume is V* (or the effluent concentration is c*) is equal to the shaded area independent of the breakthrough curve shape.

If the initially empty column is totally saturated

$$AzQ = \int_{V=o}^{V=\infty} C_o\,(1 - x)\,dV.$$

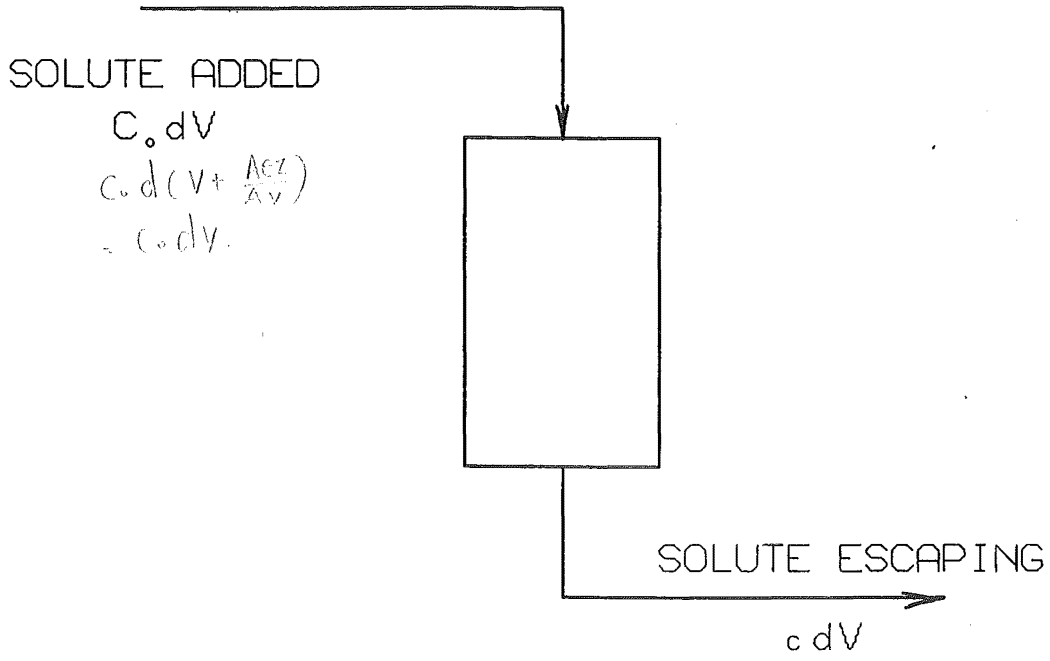
Using dimensionless variables

$$\int_{x=o}^{x=1} (1 - x)\,dZ = 1 \quad \text{or} \quad \int_{x=o}^{x=1} (1 - x)\,dT = N \tag{2-26}$$

Figure 2-4 shows that this condition is equivalent to

$$\int_{x=o}^{x=1} T\,dx = N \tag{2-27}$$

both integrals being equal to the shaded area,



IN AN ELEMENT OF TIME SUCH THAT A VOLUME dV LEAVES THE COLUMN:-

SOLUTE RETAINED WITHIN COLUMN = $(C_o - c)\,dV$

TOTAL SOLUTE RETAINED IN COLUMN = $\int_o^{V^*} (C_o - c)\,dV$

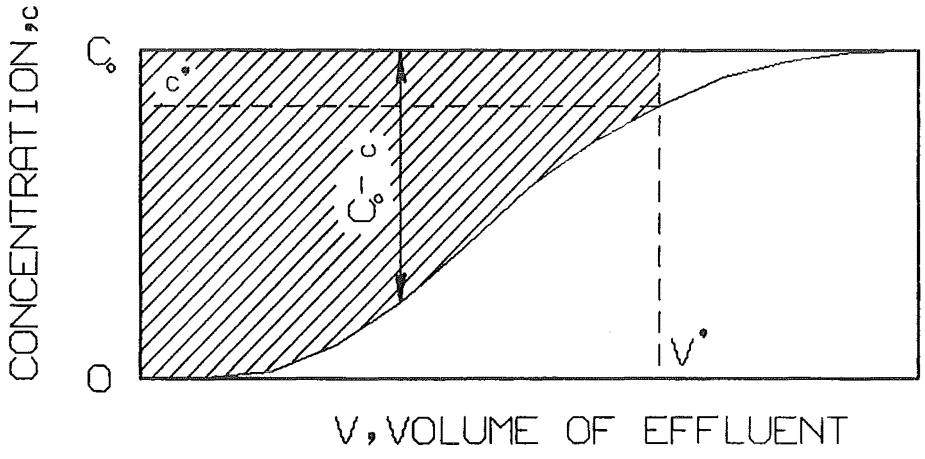
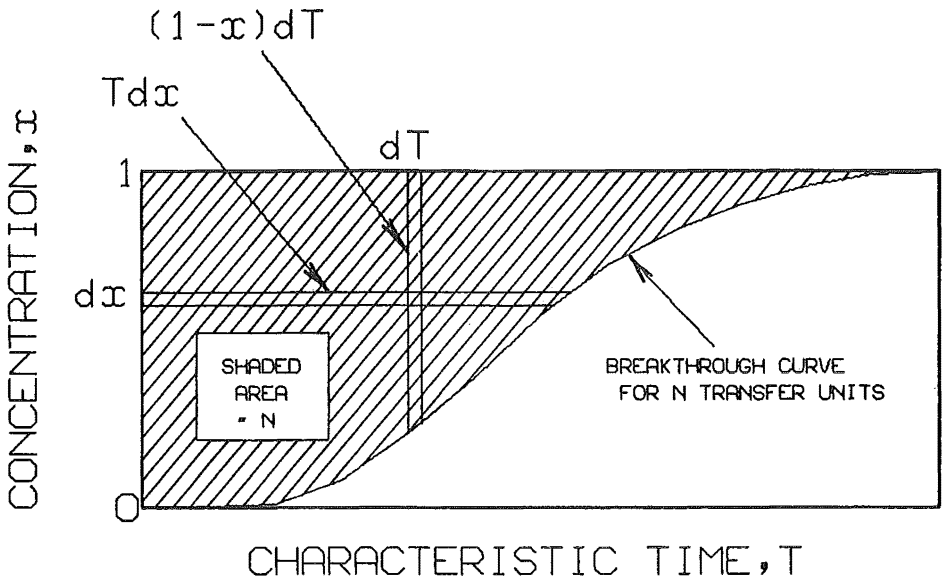


FIGURE 2-3. OVERALL MASS BALANCE.



$$\int_{x=0}^{1} T\,dx = \int_{T=0}^{\infty} (1-x)\,dT$$

FIGURE 2-4. OVERALL MASS BALANCE INTEGRAL, COMPLETELY SATURATED COLUMN

2-9. Identification of Computer Models

Three main models of the fixed bed ion exchange process have been considered in this work:-

(a) IXM (Ion exchange model-digital solution) and HIXM (Ion exchange model - hybrid computer solution).

Both film and particle (fickian form) diffusion are included, but no axial dispersion. The separation factor is constant.

(b) IXLR (Ion exchange model - linear particle rate - digital solution) and AIXLR (analog solution).

As IXM, but using the linear particle rate expression (Eqn 2.7). A modification IXVK incorporates an arbitrary separation factor dependence on concentration.

(c) HIXL (Ion exchange model, with longitudinal dispersion - hybrid solution).

As IXM, but including axial dispersion.

The equations used for each model are indicated in Table 2A-1.

APPENDIX 2A

DEVELOPMENT OF NORMALISED EQUATIONS

The particle and solution concentration ratios need to be expressed in terms of the dimensionless, independent variables, N,T,R.

2A-1. The Solution-side Basis

$N = N_f = \frac{Q\ k_f\ z}{C_o\ v}$	$T = T_f = k_f\ (t - \frac{\varepsilon z}{v})$
$\therefore \frac{\partial N}{\partial z} = \frac{Q\ k_f}{C_o\ v}$	$\therefore \frac{\partial T}{\partial z} = -\ k_f\ \frac{\varepsilon}{v}$
and $\frac{\partial N}{\partial t} = 0$	and $\frac{\partial T}{\partial t} = k_f$
$x = x(N,T)$	$\bar{y} = \bar{y}(N,T)$
$\therefore \frac{\partial x}{\partial z} = \frac{\partial x}{\partial N} \cdot \frac{\partial N}{\partial z} + \frac{\partial x}{\partial T} \cdot \frac{\partial T}{\partial z}$	
$= \frac{\partial x}{\partial N} \cdot \frac{Q\ k_f}{C_o\ v} - \frac{\partial x}{\partial T} \cdot k_f\ \frac{\varepsilon}{v}$	
and $\frac{\partial x}{\partial t} = \frac{\partial x}{\partial N} \cdot \frac{\partial N}{\partial t} + \frac{\partial x}{\partial T} \cdot \frac{\partial T}{\partial t}$	$\frac{\partial \bar{y}}{\partial t} = \frac{\partial \bar{y}}{\partial N} \cdot \frac{\partial N}{\partial t} + \frac{\partial \bar{y}}{\partial T} \cdot \frac{\partial T}{\partial t}$
$= k_f \cdot \frac{\partial x}{\partial T}$	$= k_f \cdot \frac{\partial \bar{y}}{\partial T}$

$$y = y(N,T,R)$$

$$\frac{\partial y}{\partial t} = \frac{\partial y}{\partial N} \cdot \frac{\partial N}{\partial t} + \frac{\partial y}{\partial T} \cdot \frac{\partial T}{\partial t} + \frac{\partial y}{\partial R} \cdot \frac{\partial R}{\partial t}$$

$$= k_f \cdot \frac{\partial y}{\partial T}$$

$$\frac{\partial y}{\partial r} = \frac{\partial y}{\partial N} \cdot \frac{\partial N}{\partial r} + \frac{\partial y}{\partial T} \cdot \frac{\partial T}{\partial r} + \frac{\partial y}{\partial R} \cdot \frac{\partial R}{\partial r}$$

$$= \frac{2}{d_p} \cdot \frac{\partial y}{\partial R}$$

$$\frac{\partial^2 y}{\partial r^2} = \frac{\partial}{\partial r}\left(\frac{\partial y}{\partial r}\right) = \frac{\partial}{\partial R}\left(\frac{\partial y}{\partial r}\right) \cdot \frac{\partial R}{\partial r} = \frac{\partial \left(\frac{2}{d_p} \cdot \frac{\partial y}{\partial R}\right)}{\partial R} \cdot \frac{2}{d_p}$$

$$= \frac{4}{d_p^2} \cdot \frac{\partial^2 y}{\partial R^2}$$

These differentials can be substituted into:

- The solution-side mass balance, Eqn 2-11

$$\frac{\partial x}{\partial t} + \frac{Q}{\varepsilon C_o}\frac{\partial \bar{y}}{\partial t} + \frac{v}{\varepsilon}\frac{\partial x}{\partial t} = 0$$

to give $\frac{\partial x}{\partial N} + \frac{\partial \bar{y}}{\partial T} = 0$

- the solution-side rate equation, Eqn 2-8

$$\frac{d\bar{y}}{dt} = k_f(x - x^*)$$

to give $\frac{d\bar{y}}{dT} = x - x^*$

- the linear particle-side rate expression, Eqn 2-7

$$\frac{\partial \bar{y}}{\partial t} = k_p(y^* - y)$$

to give $\frac{\partial \bar{y}}{\partial T} = \xi(y^* - y)$

- the fickian particle-side rate equation, Eqn 2-5

$$\frac{dy}{dt} = D_p\left(\frac{\partial y^2}{\partial r^2} + \frac{2}{r}\cdot\frac{\partial y}{\partial r}\right)$$

to give $\frac{\partial y}{\partial T} = \frac{\sigma}{15}\left(\frac{\partial^2 y}{\partial R^2} + \frac{2}{R}\cdot\frac{\partial y}{\partial R}\right)$.

By analogy with the linear rate expression k_p has been defined

$$k_p = \frac{60\ D_p}{d_p^2}$$

- the particle-side mass balance, differential form, Eqn 2-13

$$\frac{\partial \bar{y}}{\partial t} = \frac{6\ D_p}{d_p}\cdot\frac{\partial y}{\partial r}\Bigg|_{r\,=\,d_p/2}$$

to give $\frac{\partial \bar{y}}{\partial t} = \frac{\xi}{5}\frac{\partial y}{\partial R}\Bigg|_{R\,=\,1}$

- the integrated form of the particle-side mass balance, Eqn 2-12

$$\bar{y} = \frac{24}{d_p^3}\int_{r=o}^{r=d_p/2} r^2 y\ dr$$

to give $\bar{y} = 3\int_{R=o}^{R=1} R^2 y\ dR$

- the equilibrium relation, Eqn 2-4, is unchanged by the transformation

$$\frac{y^*}{1 - y^*} = K \cdot \frac{x^*}{1 - x^*}$$

2A-2. The Particle-side Basis

If we now define $N = N_p = \frac{Q\, k_p\, z}{C_o\, v}$

and $T = T_p = k_p(t - \frac{\varepsilon z}{v})$

an analogous development gives the following equations for the particle-side basis:-

$$\frac{\partial x}{\partial N} + \frac{\partial \bar{y}}{\partial T} = 0$$

$$\frac{\partial \bar{y}}{\partial T} = \frac{1}{\xi}(x - x^*)$$

$$\frac{\partial \bar{y}}{\partial T} = y^* - y$$

$$\frac{\partial \bar{y}}{\partial T} = \frac{1}{15}(\frac{\partial^2 y}{\partial R^2} + \frac{2}{R} \cdot \frac{\partial y}{\partial R})$$

$$\frac{\partial \bar{y}}{\partial T} = \frac{1}{5} \cdot \frac{\partial y}{\partial R}\Big|_{R=1}$$

$$\bar{y} = 3 \int_{R=o}^{R=1} R^2 y \, dr$$

2A-3. The General Equations

Table 2A-1 shows the equations for both the film- and the particle-side basis. With the introduction of the variables ρ and σ, both defined in terms of the mechanism parameter, ξ, a single set of equations can be applied to either the solution or the particle phase basis.

2A-4. The Transformed Initial and Boundary Conditions

The initial conditions correspond to an empty column, $x = 0$, $y = 0$ at $t = 0$ for $z > 0$ and all r. However, both x and y will still be zero for some time if they are some distance down the column, until solution introduced at $t = 0$ has flowed down to that depth. This takes a time $t_d = \frac{z}{v/\varepsilon}$. The characteristic time, $T = k(t - \frac{\varepsilon z}{v})$ is displaced by exactly this delay. Hence, x and y at some distance down the column

Equation	Particle Basis $\xi \leq 1$	Film Basis $\xi > 1$	General Form $0 < \xi < \infty$	Model IXLR AIXLR	IXM HIXM	HIXL	IXVK	BGP
Number of transfer units, N	$N = N_p = \frac{Q\,k_p\,z}{C_o\,v}$	$N = N_f = \frac{Q\,k_f\,z}{C_o\,v}$	$N = N_p \;\; \xi \leq 1$ $= N_f \;\; \xi > 1$	X	X	X	X	X
Characteristic Time, T	$T = T_p = ZN_p = k_p(t-\frac{\varepsilon z}{v})$	$T = T_f = ZN_f = k_f(t-\frac{\varepsilon z}{v})$	$T = T_p \;\; \xi \leq 1$ $= T_f \;\; \xi > 1$	X	X	†	X	X
Solution Mass Balance	$\frac{\partial x}{\partial N} + \frac{\partial \bar{y}}{\partial T} = 0$	$\frac{\partial x}{\partial N} + \frac{\partial \bar{y}}{\partial T} = 0$	$\frac{\partial x}{\partial N} + \frac{\partial \bar{y}}{\partial T} = 0$	X	X	†	X	†
Solution Rate Equation	$\frac{\partial \bar{y}}{\partial T} = \frac{1}{\xi}(x - x^*)$	$\frac{\partial \bar{y}}{\partial T} = x - x^*$	$\frac{\partial \bar{y}}{\partial T} = \rho(x - x^*)$	X	X	X	X	X
Linear Particle Rate Equation	$\frac{\partial \bar{y}}{\partial T} = y^* - y$	$\frac{\partial \bar{y}}{\partial T} = \xi(y^* - y)$	$\frac{\partial \bar{y}}{\partial T} = \sigma(y^* - y)$	X		X		
Fickian Particle Rate Equation	$\frac{\partial y}{\partial T} = \frac{1}{15}(\frac{\partial^2 y}{\partial R^2} + \frac{2}{R} \cdot \frac{\partial y}{\partial R})$	$\frac{\partial y}{\partial T} = \frac{\xi}{15}(\frac{\partial^2 y}{\partial R^2} + \frac{2}{R} \cdot \frac{\partial y}{\partial R})$	$\frac{\partial y}{\partial T} = \frac{\sigma}{15}(\frac{\partial^2 y}{\partial R^2} + \frac{2}{R} \cdot \frac{\partial y}{\partial R})$		X	X		X
Linear model mass balance	$\bar{y} = y$	$\bar{y} = y$	$\bar{y} = y$	X			X	
Integrated Particle Mass Balance	$\bar{y} = 3\int_o^1 R^2 y \, dR$	$\bar{y} = 3\int_o^1 R^2 y \, dR$	$\bar{y} = 3\int_o^1 R^2 y dR$		X			X
Differential Particle Mass Balance	$\frac{\partial \bar{y}}{\partial T} = \frac{1}{5} \cdot \frac{\partial y}{\partial R}\Big\vert_{R=1}$	$\frac{\partial \bar{y}}{\partial T} = \frac{\xi}{5} \cdot \frac{\partial y}{\partial R}\Big\vert_{R=1}$	$\frac{\partial \bar{y}}{\partial T} = \frac{\sigma}{5} \frac{\partial y}{\partial R}\Big\vert_{R=1}$			X		
Equilibrium	$\frac{y^*}{1-y^*} = K\frac{x^*}{1-x^*}$	$\frac{y^*}{1-y^*} = K\frac{x^*}{1-x^*}$	$\frac{y^*}{1-y^*} = K\frac{x^*}{1-x^*}$	X	X	X	‡	
	$\rho = \frac{1}{\xi}$	$\rho = 1$	$\rho = \frac{1}{\xi}, \sigma = 1$ for $\xi \leq 1$	X	X	X	X	
	$\sigma = 1$	$\sigma = \xi$	$\rho = 1, \sigma = \xi$ for $\xi > 1$	X	X	X	X	

X denotes equation used in indicated model

† denotes equation used but modified to include axial dispersion ‡ denotes a variable separation factor possible.

TABLE 2A-1. A summary of the equations and models used.

must still be zero at T = 0, and even to small values of T if equilibrium is favourable. The initial condition can be written

$$y = 0 \text{ for } T = 0, \quad N > 0, \quad 0 \leqslant R \leqslant 1.0$$

The boundary condition is straightforward, either for complete saturation

$$x = 1 \qquad T > 0, \quad N = 0$$

or for whatever partial saturation or pulse strategy is used.

CHAPTER 3

ANALYTICAL AND EMPIRICAL SOLUTIONS

The purpose of this chapter is to review some of the important analytical solutions to the fixed-bed ion exchange process.

The equations to be solved are:-

$$\frac{\partial x}{\partial N} + \frac{\partial \bar{y}}{\partial T} = 0 \qquad (3\text{-}1)$$

$$\frac{\partial \bar{y}}{\partial t} = D_p\left(\frac{\partial^2 y}{\partial r^2} + \frac{2}{r}\frac{\partial y}{\partial r}\right) \text{ or } k_p(y^* - y) \qquad (3\text{-}2a,\ 3\text{-}2b)$$

$$= k_f(x - x^*) \qquad (3\text{-}3)$$

$$\frac{y^*}{1 - y^*} = \frac{K\ x^*}{1 - x^*} \qquad (3\text{-}4)$$

$$\bar{y} = \frac{24}{d_p^3}\int_0^{d_p/2} yr^2 dr \quad \text{or } \bar{y} = y \qquad (3\text{-}5)$$

where:

C_o Total solution concentration, equivalents/litre.

d_p Particle diameter (L).

D_p Particle-phase diffusivity $(\frac{L^2}{T})$.

k Mass transfer coefficient; particle phase k_p, or solution-phase k_f (T^{-1}).

N Number of transfer units; particle phase $N_p = \frac{Q\ k_p\ z}{C_o\ v}$ or solution phase $N_f = \frac{Q\ k_f\ z}{C_o\ v}$.

Q Resin capacity, equivalents per litre of packed column.

r Radial distance in particle (L).

t Time, measured from application of feed solution to column (T).

T Characteristic time; based either on the particle phase $(T_p = ZN_p)$ or on the solution phase $(N_f = ZN_f)$.

v Solution superficial velocity $(\frac{L}{T})$.

x Solution concentration ratio.

y Concentration ratio at any point in the particle.

$\bar{y}$ Average concentration ratio over the particle.

x^*, y^* Interfacial and/or equilibrium concentration ratios.

z Bed depth (L).

Z Throughput ratio, $\frac{C_o v(t - \frac{\varepsilon z}{v})}{Qz}$.

ε Voidage.

ξ Mechanism parameter, N_p'/N_f'.

Breakthrough curves (plots of x against T) are required. These depend on N_p, N_f and K, or ξ, N and K according to the choice of variables. The methods of this chapter with one exception are concerned with the prediction of a single breakthrough curve carried to completion - cyclic operation is not considered.

Analytical solutions are difficult to obtain for the general case because of the non-linear equilibrium relation (Eqn 3-4) and because of the variable coefficient in equation 3-2a. Modifications to the equations have been made, corresponding to more-or-less tenable physical assumptions, and can be summarised as follows:

1. Equilibrium assumptions

(a) Unfavourable equilibrium, $K < 1$, reduces the significance of mass transfer limitations.

(b) Linear equilibrium, $K = 1$, removes the nonlinearity of Eqn 3-4 from the problem.

(c) Favourable equilibrium, $K > 1$, presumes that a balance is established between dispersion due to mass transfer resistance and sharpening due to favourable equilibrium.

(d) Very favourable equilibrium, with the separation factor infinite, implying that $y^* = 1$ and reducing the fixed bed process to a modification of batch operation.

2. Rate assumptions

(a) No rate limitations, hence equilibrium operation as 1(a).

(b) All rate effects included in an axial dispersion term and bulk-phase equilibrium.

(c) Resistance predominantly in one phase; either film or particle mass transfer only need be considered. Often this has little advantage because the nonlinear Eqn 3-4 remains unless a further assumption is taken from class 1.

(d) Empirical rate expressions may allow mathematical simplicity

at the cost of reduced physical correspondence and correlation.

3. Mass balance assumptions

(a) No axial dispersion, an assumption already made in Eqn 3-1.

(b) Constant pattern assumption replaces the mass balance, Eqn 3-1, with the simple relation $x = y$.

4. Staged approximations

The distributed partial differential equations can be approximated by a lumped set of ordinary differential equations. Physically this corresponds to sectioning the column into plates.

The material of this chapter has been included because of its importance, either practical or historical, particularly if useful for verification of numerical or computer solutions. More complete reviews have been presented by Vermeulen (1958); Hiester, Vermeulen and Klein (1963); and Lightfoot, Sanchez-Palma and Edwards (1962); while Vermeulen and Hiester (1959) have presented a tabulation relating the available solutions to their assumptions.

The following chapter surveys in some detail computer solutions to the ion exchange equations. The distinction between the "non-computer" solutions of this chapter and the mechanised results of later chapters is hard to draw. Any analytical solution

$$f(x, T, N, \xi, K)$$

can be programmed for computer evaluation. Any computer solution can be performed by hand with sufficient persistance.

The distinction drawn here is in terms of explicitness and generality. This chapter is concerned with breakthrough curve expression in the form

$$x = x(T, N, \xi, K) \quad \text{or} \quad T = T(x, N, \xi, K)$$

and with some restriction or assumption in the model to allow this.

For example, both Rosen's solution and the Thomas solution are included in this chapter since both can be expressed in the form

$$x = \int g(N, T, \xi, K, \lambda)\, d\lambda$$

although the integral is best evaluated numerically, and by computer.

3-1 Equilibrium Solutions

Under conditions of high mass transfer rates in both the liquid and solid phases and unfavourable equilibrium, concentration gradients will be small across the interface. The bulk phase concentrations will consequently tend to be in equilibrium. The required conditions are those typically pertaining during regeneration of an ion exchange column.

The basic equation (De Vault, 1943)

$$\frac{dy}{dx} = Z + \frac{A}{N} \tag{3-6}$$

was derived by integrating the mass balance (Eqn 3-1) leaving the arbitrary constant A to be evaluated by the overall mass balance, Eqn 2-26. Using the normal ion exchange isotherm, Eqn 3-4 (others have been used, Wilson, 1940; Weiss, 1943), the proportionate pattern result follows:-

$$Z = \frac{K}{[1 + (K - 1)x]^2} \quad \text{or} \quad x = \frac{1 - \sqrt{\frac{K}{Z}}}{1 - K} \tag{3-7}$$

so-called because the width of the breakthrough curve (or pattern), given by $\frac{1}{K} - K$ (Figure 3-1), is proportional to the volume of feed added, i.e. as the solute front passes through the column it becomes proportionately more diffuse, hindering sharp separation.

The equation is self-protective with regard to violation of its assumption of unfavourable equilibrium in that the width of the breakthrough curve becomes zero for $K = 1$, and negative for $K > 1$. This is in physical accord, since, with no dispersive effects, the breakthrough curve must be a vertical line at $z = 1.0$ (Boyd, 1947).

Vermeulen (1958, page 174) has compared equilibrium-limited behaviour with the more general results available from the Thomas equation (Eqn 3-23). The proportionate pattern limit is approached only for a large number of transfer units, more than 500 being required at $K = 0.5$. Figures 3-2, 3-3 and 3-4 from Kelly et al. (1970) compare experimental results with the proportionate pattern result, supporting Vermeulen's contention. For columns of common industrial size, the proportionate pattern predictions are not likely to be reliable, especially near the sharp discontinuity at $x = 0$.

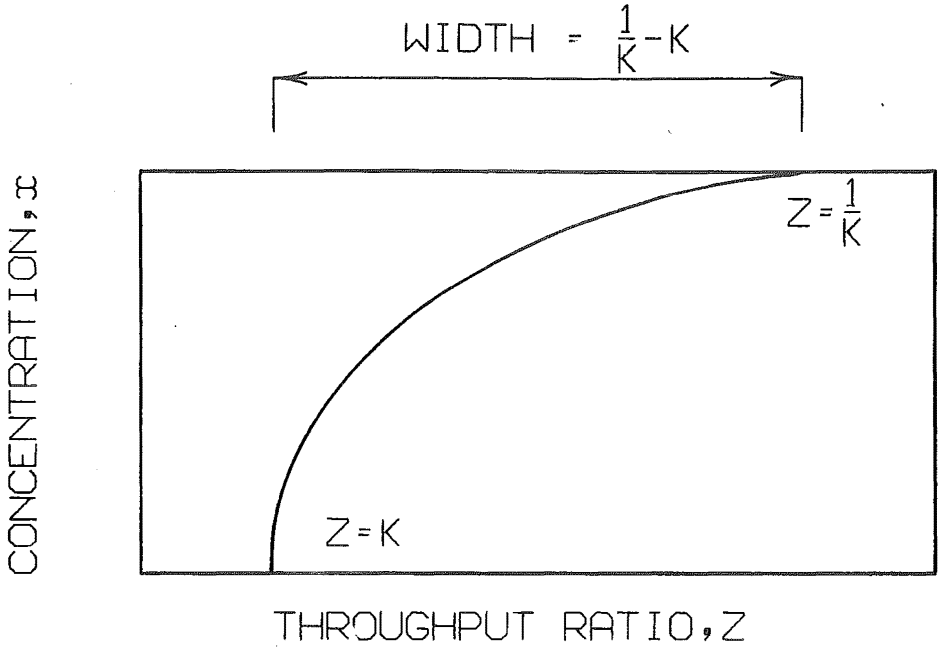


FIGURE 3-1. PROPORTIONATE PATTERN SOLUTION FOR ION EXCHANGE.

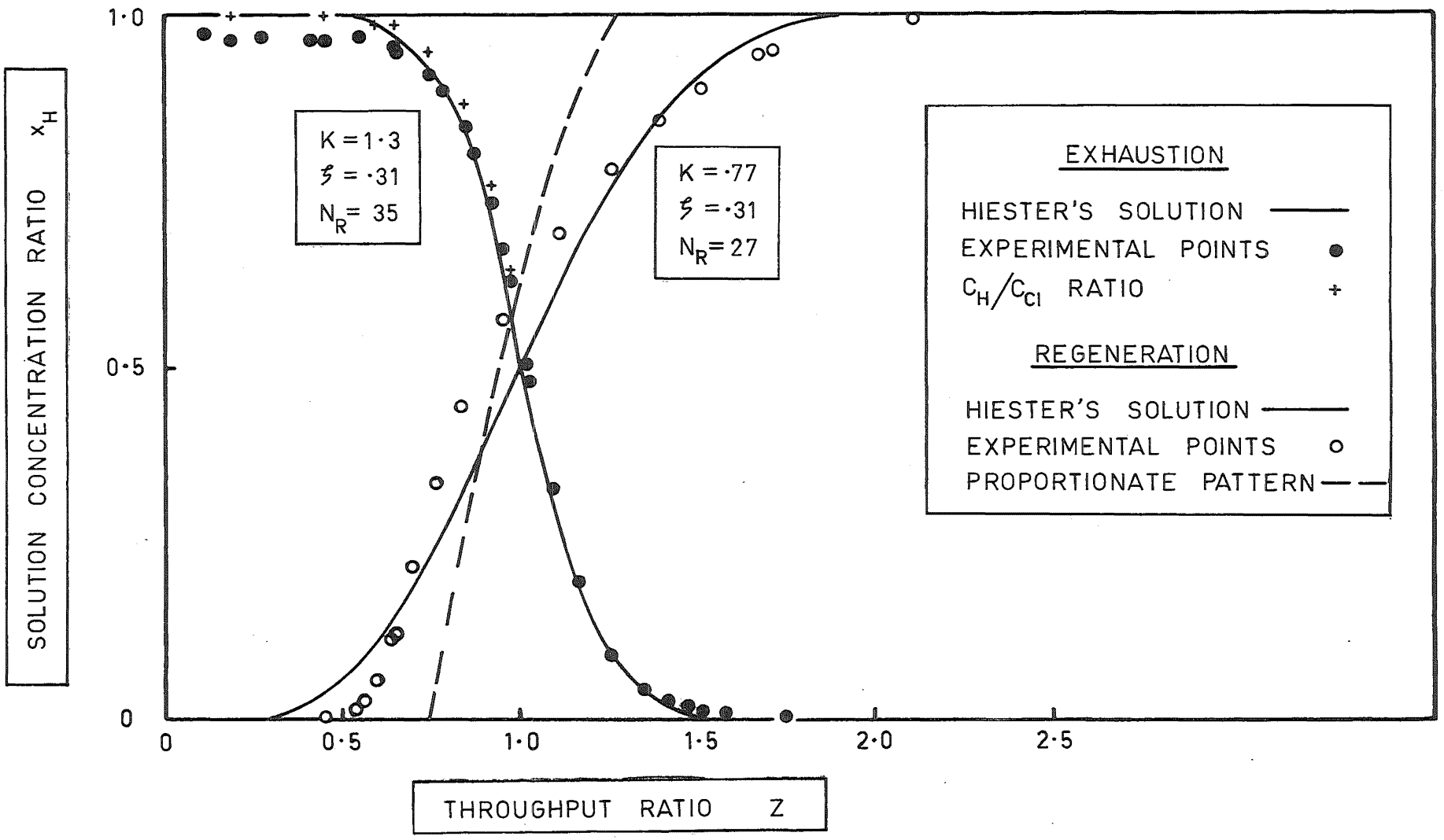
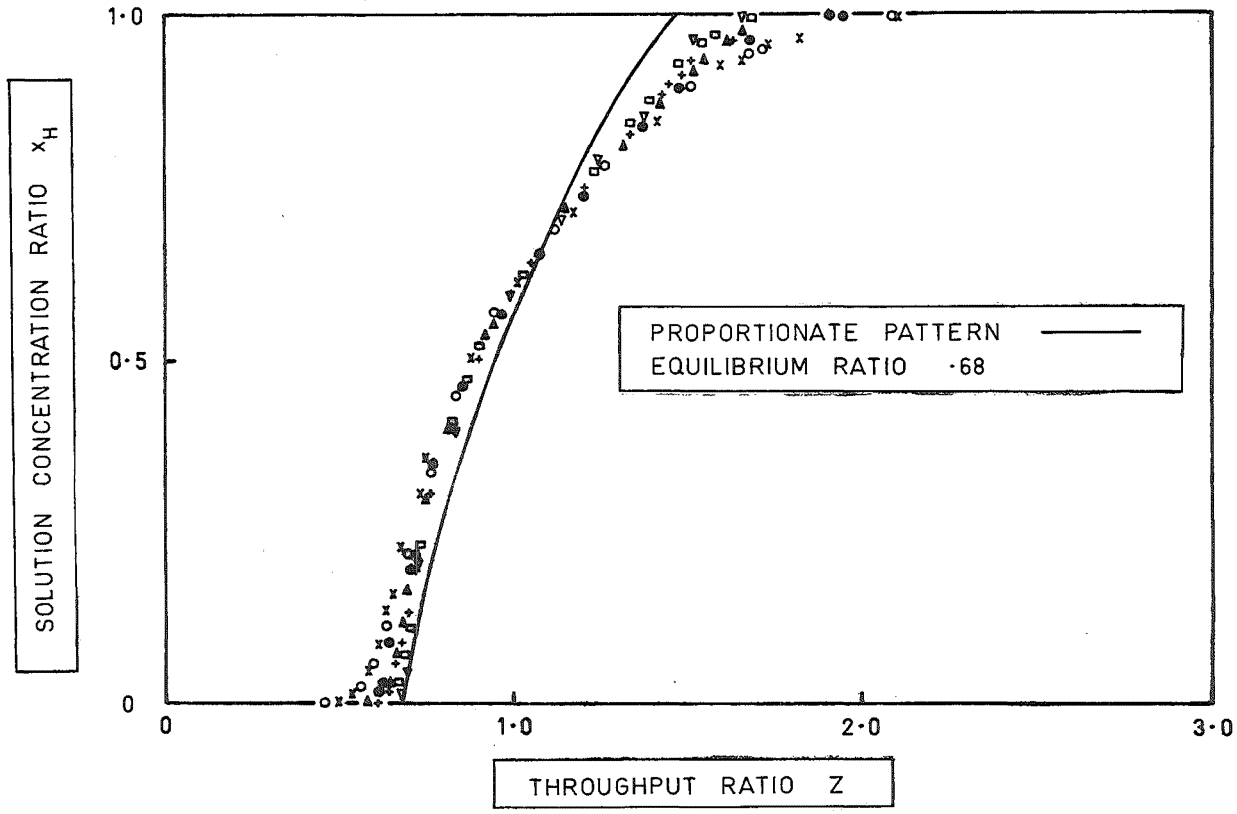


FIGURE 3-2. THE PROPORTIONATE PATTERN SOLUTION AND EXPERIMENTAL RESULTS.



	○	×	●	▲	+	□	▽
NORMALITY	1·0	0·1	0·1	0·1	0·1	0·1	0·1
EQUILIBRIUM RATIO	·77	·68	·68	·68	·68	·68	·68
BED CAPACITY, MEQ	1355	435	905	1355	1830	1355	1355
FLOW RATE, ML/MIN	52	52	52	52	52	26	13

FIGURE 3-3. THF PROPORTIONATE PATTERN SOLUTION AND EXPERIMENTAL RESULTS.

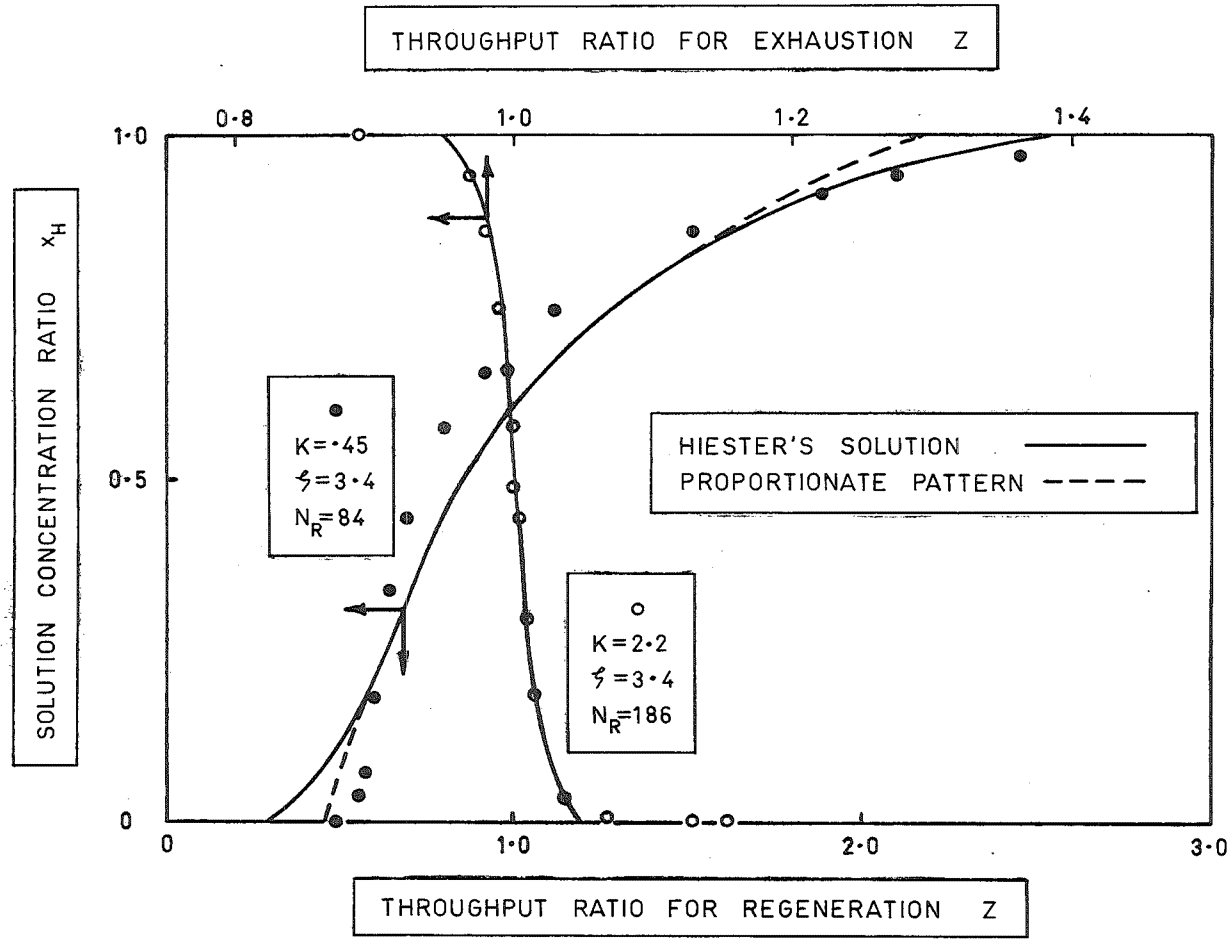


FIGURE 3-4. THE PROPORTIONATE PATTERN SOLUTION AND EXPERIMENTAL RESULTS.

More recently, the bulk equilibrium assumption has been used to widen the range of adsorption operations susceptible to analysis.

Klein (1967), supplemented by Helfferich (1967), has produced a numerical solution for multicomponent, fixed bed adsorption with this assumption, but allowing varying separation factors. An analytical solution (Tondeur and Klein, 1967) is possible for constant separation factors. Tondeur (1970) has developed the work to include "activity inversion", the multicomponent analog of Reichenberg's observations of concentration effects on binary separation factor values to such an extent that selectivity can be reversed.

Amundson (1965) has used the assumption of bulk equilibrium and the mathematics of wave theory to analyse fixed-bed, single-solute, adiabatic adsorption. Significant concentration effects resulted from the temperature dependence of the benzene vapour-carbon isotherm.

3-2. Linear Equilibrium

A linear equilibrium isotherm, for which the equilibrium concentration in the solid is proportional to the solution concentration, implies $x^* = y^*$, corresponding to $K = 1$ in the ion exchange equilibrium expression (Eqn 3-4). Analytical solutions become more likely as the nonlinearity in this equation is removed.

Linear equilibrium is not common in ion exchange since the exchanging ions are physically different and are unlikely to be equally attracted to the resin matrix; the principal exception is isotopic exchange. Fixed-bed applications with linear equilibrium are common in chromatographic separations of dilute mixtures, and in the well-investigated case of regenerative heat transfer.

Schumann (1929) and Angelius (1926) independently analysed the transfer of heat from a flowing fluid to a stationary bed of particles, with the following assumptions:-

- constant fluid flow rate
- plug flow
- no axial dispersion
- temperature-independent system properties
- no conduction in the solid or the fluid

- only film-side resistance to heat transfer, with a linear temperature driving force
- no heat loss from the sides of the bed.

Schumann made the common transformation of the independent variables

$$T = k_f\left(t - \frac{\epsilon z}{v}\right) \quad \text{and} \quad N = \frac{Q\, k_f\, z}{C_o\, v}$$

Further substitution for the dependent variables reduces the equation to be solved to the form

$$\frac{d^2V}{d_p^{\,2}} + \frac{1}{p}\frac{dV}{d_p} + V = 0 \qquad (3\text{-}8)$$

which has a solution in terms of a modified Bessel function of the first kind, normally expressed (Thomas, 1944) in terms of the J function

$$J(x,y) = 1 - \int_0^x \exp(-y - t)\, I_o\, (2\sqrt{yt})\, dt \qquad (3\text{-}9)$$

where I_o is the modified Bessel function of order zero. The solution of the problem in terms of the original variables is:-

$$x = J(N, T) \qquad (3\text{-}10)$$

$$y = 1 - J(T, N)$$

Tabulations of this function are available (Helfferich, 1962) which are more accurate, especially for small J, than are the graphical presentations (Heister and Vermeulen, 1952). Appendix 3A contains a computer program for the evaluation of this function which has been developed because of a small number of misprints in Helfferich's table and to avoid the problems of interpolation. A number of explicit approximations are available (Vermeulen, 1958, page 180).

Although the J function solution was derived for film mass transfer control, the assumption of linear equilibrium allows any linear rate equation to be used equivalently, Table 3-1.

Rate Mechanism	Rate Equation	Relations	Result
Particle control, linear rate	$\frac{dy}{dt} = k_p(y^* - y)$	$x = x^*$ $x^* = y^*$ $\therefore x = y^*$	$\frac{dy}{dt} = k_p(x - y)$
Film control	$\frac{dy}{dt} = k_f(x - x^*)$	$y^* = y$ $x^* = y^*$ $\therefore x^* = y$	$\frac{dy}{dt} = k_f(x - y)$
Mixed control	$\frac{dy}{dt} = k_p(y^* - y)$ $= k_f(x - x^*)$ $= k_R(x - y)$	$\frac{1}{k_R} = \frac{1}{k_f} + \frac{1}{k_p}$	$\frac{dy}{dt} = k_R(x - y)$
Reaction kinetics	$\frac{dy}{dt} = k_R\left[x(1-y) - \frac{y(1-x)}{K}\right]$	$K = 1$	$\frac{dy}{dt} = k_R(x - y)$

TABLE 3-1. The equivalence of the linear rate equations with linear equilibrium.

Rosen (1952b,1954) has provided an explicit, linear-equilibrium solution including film diffusion and particle diffusion (fickian form) in terms of an integral which must be graphically, mechanically (Rosen, 1952a)or numerically evaluated. The difficulty in the analysis is that the interfacial concentration, y*, increases gradually with the increase in solution concentration whereas an analytical result is available for the concentration at any point in the particle for a step change in y*. However, Rosen has related these two circumstances using Duhamel's theorem. Integration over the particle gives the average particle concentration which can be differentiated with respect to time to give the rate, $\frac{\partial \bar{y}}{\partial t}$. When substituted into the solution mass balance, and the partial differential equation solved using Laplace transform methods, the required solution in x is obtained.

Rosen (1954) has provided numerical solutions for a number of breakthrough curves and also suggested an approximate, easily used expression

$$x = \tfrac{1}{2}\left(1 + \operatorname{erf}\left(\frac{T - N}{2\sqrt{N}}\right)\right) \qquad (3\text{-}11)$$

applicable for film control.

Babcock et al. (1966) have extended Rosen's analysis to include axial dispersion (chapter 9).

These powerful analytical results are limited in their usefulness for ion exchange because of the assumption of linear equilibrium. However, they are most useful for the purposes of this thesis in verifying the results of numerical computations.

Even with this assumption, the derivation of working equations for fixed-bed operations is extremely difficult. Further, the use of the working equations can be impracticably laborious (Lapidus and Amundson, 1952). A numerical, finite-difference solution of the basic equations may be more efficient than the evaluation of difficult integrals.

3-3. Favourable Equilibrium (Constant Pattern).

Under favourable equilibrium, $K > 1.0$, breakthrough curves for beds of increasing depth become geometrically similar, differing only in placement (Figure 3-5). This implies that the column concentration profiles are also invariant. The physical explanation is that the spread of the reaction zone caused by the slowness of mass transfer, and perhaps the neglected effects of longitudinal dispersion and flow maldistribution, are balanced by the tendency of the favourable equilibrium to produce an abrupt front (Glueckauf, 1947).

Vermeulen (1958) reports that Dryden (1951) was the first to use the term "Constant pattern" to describe the invariant form, appropriate because the width of the breakthrough curve or "pattern" is independent of bed depth or volume added to the column.

Bohart and Adams (1920) working on the adsorption of chlorine on charcoal for design of gas-masks, investigated the effect of pressure and temperature, and more significantly, fluid velocity and bed-length. Their experimental results indicated constant pattern conditions. An analytical expression was derived for such conditions with irreversible adsorption and a first-order kinetic rate expression. Further experimental evidence for constant pattern conditions was provided by Wicke (1939) working with mixtures of nitrogen and carbon dioxide on active carbon.

Sillén (1946) considered Eqn 3-1 with an irreversible, second-order reaction kinetic expression and showed that the resultant expression reduced to a constant pattern form for large t. Other rate expressions were considered, including the reversible second-order reaction kinetic expression (Section 3-4) (Sillén and Ekedahl, 1946), and analytical solutions could be obtained if constant pattern conditions were assumed.

Table 3-2 presents a number of constant pattern solutions for irreversible adsorption ($K = \infty$) and various rate laws.

The quadratic rate expression in Table 3-2 is an attempt (Vermeulen, 1953; Glueckauf, 1955), to provide a better approximation to the fickian diffusion expression (Eqn 3-2a) than the linear rate equat-

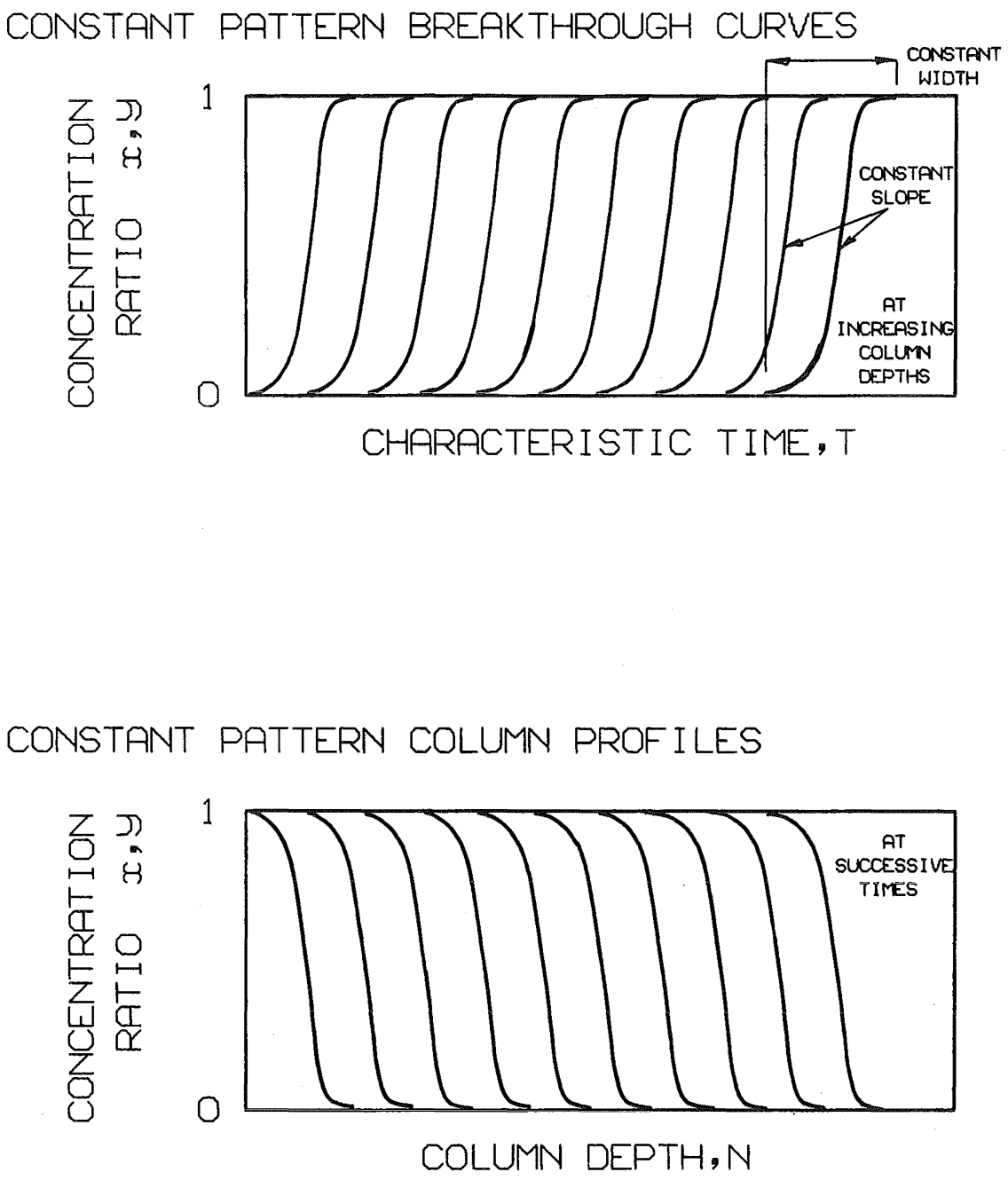


FIGURE 3-5. CONSTANT PATTERN CONCENTRATION CURVES.

Rate Mechanisms	Solution	Reference
Film diffusion		
$\frac{dy}{dT} = x - x^*$	$x = \exp(T - N - 1)$	Drew, Spooner, Douglas
Particle diffusion		
(a) Linear rate, $\frac{dy}{dT} = y^* - y$	$x = 1 - \exp[-(T - N + 1)]$	Glueckauf and Coates (1947)
(b) Quadratic rate, $\frac{dy}{dT} = \frac{y^{*2} - y^2}{2y}$	$x = 1 - \exp[-\frac{\pi^2}{15}(T - N) - 0.61]$	Vermeulen (1953)
(c) Fickian diffusion, $\frac{dy}{dT} = \frac{\partial^2 y}{\partial r^2} + \frac{2}{r}\frac{\partial y}{\partial r}$	$x = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp[-n^2\lambda]$ where $\lambda = \frac{\pi^2}{15}(T - N) + 0.64$	Wicke (1939)
Reaction kinetics		
$\frac{dy}{dT} = x(1 - y)$	$x^{-1} = 1 + \exp[-(T - N)]$	Bohart and Adams (1920) Sillén (1946)

TABLE 3-2. Constant pattern solutions - irreversible equilibrium.

ion (Eqn 3-2b). If the solution of Eqns 3-2a and 3-2b are compared for irreversible adsorption (implying constant surface concentration), then the agreement is not good. Vermeulen shows that

$$y^2 = 1 - \exp(-T)$$

is a better approximation. Differentiation of this approximation gives the rate expression

$$\frac{dy}{dt} = k_p \left(\frac{1 - y^2}{2y}\right) \tag{3-12}$$

This quadratic driving force expression is applied to irreversible adsorption by introducing the surface concentration, y^*, which is now time-varying. A further factor $\psi \left(= \frac{\pi^2}{15}\right)$ is introduced so that the solutions given by

$$\frac{dy}{dt} = k_p \psi \frac{y^{*2} - y^2}{2y} \tag{3-13}$$

match Rosen's results for linear equilibrium. Glueckauf (1955) has used this factor to include some correction for reversible equilibrium

$$\psi = \frac{K\pi^2}{\pi^2 + 15(K - 1)} \tag{3-14}$$

Cooper (1965) using analytical and numerical methods has solved the equations for particle control with irreversible equilibrium and a number of rate expressions. A limiting solution was rigorously derived for the linear rate expression, applicable for $N_p > 1$ (compare $N_p > 4$, Table 3-4). No limiting solution could be analytically demonstrated for other rate expressions but presumably one would have become apparent if the graphs of breakthrough curves had been continued to larger values of N_p.

If the equilibrium is favourable but reversible, a series of constant pattern solutions is possible for various rate expressions, Table 3-3. These equations were derived by a variety of methods, for instance, Michaels (1952) considered a fixed-bed as part of an infinitely high countercurrent column.

However, a more general approach is possible. If the concentration ratio is x at some point P in the bed, then for constant pattern conditions, P (and all other points corresponding to other solution con-

Rate Mechanism	Solution	Reference
Film diffusion		
$\frac{dy}{dT} = x - x^*$	$\frac{K}{K-1}\ln x - \frac{1}{K-1}\ln(1-x) = T - N + \alpha_f$	Michaels (1952) Lapidus and Rosen (1954)
Particle diffusion		
(a) Linear rate, $\frac{dy}{dT} = y^* - y$	$\frac{1}{K-1}\ln x - \frac{K}{K-1}\ln(1-x) = T - N + \alpha_p$	Glueckauf and Coates (1947)
(b) Quadratic rate, $\frac{dy}{dT} = \frac{y^{*2} - y^2}{2y}$	$\frac{K}{K-1}\ln\frac{1}{1-x} - \frac{K}{K+1}\ln\left[\frac{K(1+x) + (1-x)}{K-1}\right] + \frac{2\ln x}{(K-1)(K+1)} = T-N + \alpha_q$	Vermeulen (1953) Hall et al. (1966)
(c) Fickian diffusion, $\frac{dy}{dT} = \frac{\partial^2 y}{\partial R^2} + \frac{2}{R}\frac{\partial y}{\partial R}$	Not available analytically.	Hall et al. (1966)
Reaction kinetics		
$\frac{dy}{dT} = x(1-y) - \frac{(1-x)y}{K}$	$\frac{K}{K-1}\ln\frac{x}{1-x} = T - N$	Walter (1945) Sillén (1946)

TABLE 3-3. Constant pattern solutions - favourable equilibrium with constant separation factor.

centration ratios) must move with constant velocity, to preserve the "constant pattern";

$$\left.\frac{\partial N}{\partial T}\right|_x \quad \text{is a constant.}$$

By the mass balance relation (Eqn 3-1), $\left.\frac{\partial x}{\partial y}\right|_{N,T}$ must also be constant. Integrating this equation, with the conditions:-

$$x = 0 \quad \text{at} \quad y = 0$$

$$x = 1 \quad \text{at} \quad y = 1$$

then the constant pattern condition results:-

$$x = y \tag{3-15}$$

replacing a differential equation with an algebraic equation.

The velocity, v_f, of the solution concentration profile (or the point P) is given by

$$v_f = \frac{v}{1 + \frac{Q}{\varepsilon C_o}}$$

If the rate expression is of the form

$$\frac{d\bar{y}}{d\bar{T}} = a(x,y) \tag{3-16}$$

then the breakthrough curve is (Lapidus and Rosen, 1954)

$$\int_{x_1}^{x} \frac{dx}{a(x,x)} = T - T_1 - N \tag{3-17}$$

where (x_1, T_1) is a point on the breakthrough curve. The breakthrough curve may be located by evaluating T_1 (or the equivalent constants, α_p, α_q, α_f, in Table 3-3) by the overall mass balance (Eqn 2-27). The constants α_p and α_f have been evaluated by numerically integrating this equation (Hiester et al., 1963, Table 16-9) giving the results of Table 3-4. However, Appendix 3B shows that this integration can be done analytically and that the correct values should be:-

$$\alpha_p = 1$$

$$\alpha_f = -1 \tag{3-18}$$

$$\alpha_q = 2 + \frac{K}{K-1}\left[\ln\frac{K+1}{K-1} - \frac{2K}{K+1}\ln\frac{2K}{K-1}\right]$$

The error in using the incorrect α_p or α_f values is small, being worst at low K and N values. These will not be conditions for which constant pattern operation will be likely.

Analytical constant pattern solutions for fickian diffusion are not available; Eqn 3-2a is not of the form of Eqn 3-16. However, Hall et al. (1966) have produced a set of generalised charts from a numerical solution for this diffusion expression, and also for pore diffusion. In both cases, a solution of the parabolic partial differential equation

$$A. \frac{\partial x}{\partial \bar{T}} = \frac{\partial^2 x}{\partial R^2} + \frac{2}{\bar{R}} \frac{\partial x}{\partial R}$$

is required, where $A = \dfrac{15.0K}{[1 + (K-1)x]^2}$ for pore diffusion

or $A = 15.0$ for particle diffusion.

Matching mid-point slopes from this solution with that using the quadratic driving force rate expression allowed further refinement of the correction factor ψ to

$$\psi = \frac{K^{3/2}}{1 + 1.688 \sqrt{K}(K - 1)}$$

At intermediate values of the mechanism parameter ($0.3 < \xi < 3.0$) where mass transfer resistance is distributed and cannot be lumped into either phase, the constant pattern assumption has not so far produced any solution. Hall et al. have however derived an analytical solution for mixed film and pore diffusion at irreversible equilibrium:-

$$T - N = \frac{15}{\sqrt{3}} \left[\tan^{-1}\left(\frac{2p + 1}{\sqrt{3}}\right) - \frac{\pi}{6}\right] - \frac{15}{2}\left[\ln(1 + p + p^2) - \frac{1}{3}\right] + \frac{N_{pore}}{N_F} \ln(x + 1) \qquad (3\text{-}19)$$

where $p = (1 - x)^{1/3}$. Pore diffusion is important to many adsorption processes, but not to ion exchange using conventional gel-type resins. Recent publications have included an approximate rate equation (Vermeulen and Quilici, 1970) and analytical results for irreversible equilibrium (Cooper and Liberman 1970).

3-3-1 Development of Constant Pattern

Constant pattern breakthrough curves will be asymptotically approached for favourable equilibrium in sufficiently long beds. Rosen (1952a) has proved the existence and uniqueness of constant pattern profiles for either particle or film mass transfer resistances, or both combined. Cooney and Lightfoot (1965) have similarly shown that constant pattern solutions will still occur with significant axial dispersion, although the x = y condition no longer applies. It still remains to find these solutions, even if they have been shown to exist, and further to establish how quickly the asymptotic form is established.

The general recommendations of Hiester et al. (1963) for the minimum number of transfer units, N_{min}, required for constant pattern conditions to be established are included in Table 3-4. These were obtained by comparing constant pattern solutions with the more general but less rigorous reaction-kinetic solution (Section 3-4).

3-3-2 Experimental Verification of Constant Pattern Results

The attainment of a constant pattern is not easy to establish from experimental results. The equality of x and y is a useful test when dealing with computer-generated breakthrough curves, but not for experimental results as resin concentrations are not easily sampled or determined. The width of the breakthrough curve will be constant at constant pattern, but this is difficult to determine sufficiently accurately with interpolated point data. The mid-point slope is also constant at constant pattern and most commonly used, notwithstanding the problems of differentiating experimental data and the accuracy required.

Kelly (1966) did not attain constant pattern profiles for the Na - H - Cl system (K = 1.3, N_R = 14 to 35) supporting the recommendations of Table 3-4 which indicates N_{min} = 50.

Lapidus and Rosen (1954) present experimental results for Na - H - Cl for various bed depths with Dowex-50 (both 4 and 8 % DVB) and C_o = .173 and .083N with the separation factor 2.7. The data correspond well with constant pattern predictions for N_F greater than

K	α_p	α_f	N_{min}
∞	1.0	-1.0	4
5.0	1.05	-1.10	10
2.0	1.14	-1.17	25
1.2	1.17	-0.69	75

TABLE 3-4. Constant pattern constants (incorrect) and limits, Hiester et al. (1963).

24 to 35, depending on degree of cross-linking. Table 3-4 suggests that about 18 transfer units should be sufficient.

The constant pattern assumption has also been applied to multi-component separations; Cooney and Lightfoot (1966), have shown that ion exclusion results could be well represented using constant pattern, and that while this did not lead to analytical expressions, dramatic reductions in computer time did result (11 seconds against half an hour).

The experiments of Leavitt (1962) working with the adsorption of carbon dioxide from nitrogen in large columns and the analysis of Pan and Basmadjian (1967) both indicate that constant pattern occurs under adiabatic conditions, both for the concentration and the temperature profiles.

3-4 Reaction Kinetic Rate Expressions

Non-equilibrium in ion exchange operations is explained by diffusional resistances in the particle and the resin. The problems of providing a general, analytical solution for all but the most simple systems are intractible. Mathematical convenience and significant advances can be made if the diffusion mechanism be replaced by an arbitrary kinetic rate expression for a reversible, bimolecular reaction:-

$$\frac{dy}{dt} = k_R \left[x(1 - y) - \frac{1}{K} y(1 - x)\right] \qquad (3\text{-}20)$$

where k_R is a reaction rate constant.

For linear equilibrium, K = 1, the expression reduces to $\frac{dy}{dt} = k_R(x - y)$, analogous to the film or particle control expressions in Section 3-3 and a corresponding definition can be used for the number of reaction transfer units in a packed column

$$N_R = \frac{Q\, k_R\, z}{C_o\, v} \quad . \qquad (3\text{-}21)$$

Reaction kinetic results for constant pattern conditions have already been mentioned (Section 3-2). Thomas (1944) was able to generalise these outside constant pattern conditions and to non-

linear equilibrium. Since the solution mass balance can be put in the form

$$\frac{\partial x}{\partial N_R} + \frac{\partial y}{\partial T_R} = 0$$

then by the definition of a perfect differential (Piaggio, 1958) there is some function f(N,T) such that

$$df = \frac{\partial f}{\partial N} dN + \frac{\partial f}{\partial T} dT = x\, dN - y dT$$

where $x = \frac{\partial f}{\partial N}$, $y = -\frac{\partial f}{\partial T}$. If a rate law applies in the form

$$\frac{dy}{dT} = F(x,y)$$

and $\frac{\partial y}{\partial T} = \frac{\partial}{\partial T}(-\frac{\partial f}{\partial T}) = -\frac{\partial^2 f}{\partial T^2}$

then $\frac{\partial^2 f}{\partial T^2} + F(\frac{\partial f}{\partial N}, -\frac{\partial f}{\partial T}) = 0$

This equation is non-linear unless the rate law, F, is first order. However, the substitution

$$f(N,T) = C \ln \{G(N,T) \cdot \exp[-(AN + BT)]\} \qquad (3\text{-}22)$$

where A,B,C are constants, leads to

$$\frac{\partial^2 G}{\partial N \partial T} - A \cdot B \cdot G(N,T) = 0$$

which can be solved by the method of characteristics. After considerable manipulation the solution can be expressed in terms of the J function, developed as a solution for linear equilibrium. Laplace transform methods have also been used (Goldstein, 1953).

$$x = \frac{J(\frac{N_R}{K}, T_R)}{J(\frac{N_R}{K}, T_R) + [1 - J(N_R, \frac{T_R}{K})] \cdot \exp[-(\frac{K-1}{K})(T_R - N_R)]} \qquad (3\text{-}23)$$

$$y = \frac{1 - J(T_R, \frac{N_R}{K})}{J(\frac{N_R}{K}, T_R) + [1 - J(N_R, \frac{T_R}{K})] \cdot \exp[-(\frac{K-1}{K})(T_R - N_R)]}$$

This equation is important because:-

(a) It is quite general, applicable for all values of the separation factor, with N_R being related to either N_p or N_f (or both for the case of mixed control) by the work of Hiester, Vermeulen and others (1956).

(b) Other less general equations can be derived:

- linear equilibrium results for all linear rate expressions
- constant pattern solution for the kinetic rate expression
- the proportionate pattern solution

(c) Further generalisations have been obtained for uniform partial presaturation, Vermeulen (1954), and more doubtfully for varying N_R or K (Vermeulen 1958, p. 190).

The relation between N_R, the number of reaction transfer units and the number of solution and/or particle transfer units has been provided by Hiester et al. (1956) through the equation

$$\frac{b}{N_R} = \frac{1}{N_p} + \frac{1}{N_f} \qquad (3\text{-}24)$$

where

$$b = \frac{(x - x^*) + (y^* - y)}{x(1-y) - \frac{y(1-x)}{K}}$$

The equation applies exactly for linear equilibrium (b = 1). Approximate values of b have been suggested to correct for non-linear equilibrium assuming limiting behaviour (K > 1, constant pattern; K < 1, proportionate pattern) for particle or film control:-

	Particle Control	Film Control
K < 1	$b = \frac{2K}{K + 1}$	$b = \frac{K + 1}{2}$
K > 1	$b = \frac{2K}{K + 1}$	$b = \frac{2K}{K + 1}$

For mixed diffusion, Hiester et al. have correlated experimental results to establish values of b for all conditions (Figure 3-6).

The calculation of breakthrough curves using this method is summarised in Fig. 3-7 and Appendix 3C.

Vermeulen and Hiester (1959) have also contributed to the inverse problem of estimating N_R from experimental breakthrough curves (reproduced in Fig. 3-8) relating the midpoint slope with N_R at values of the separation factor.

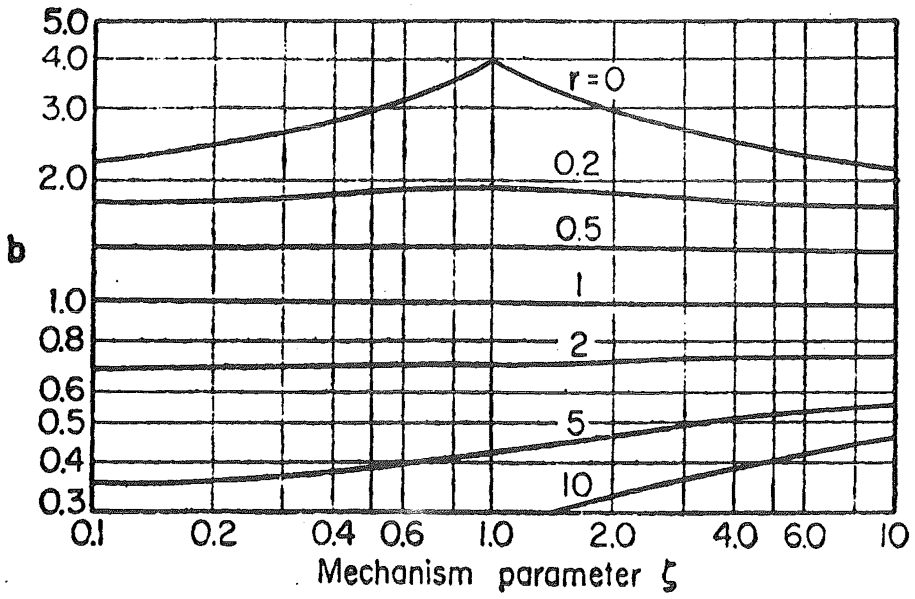


FIGURE 3-6. THE CORRECTION FACTOR b FOR NON-LINEAR EQUILIBRIUM.

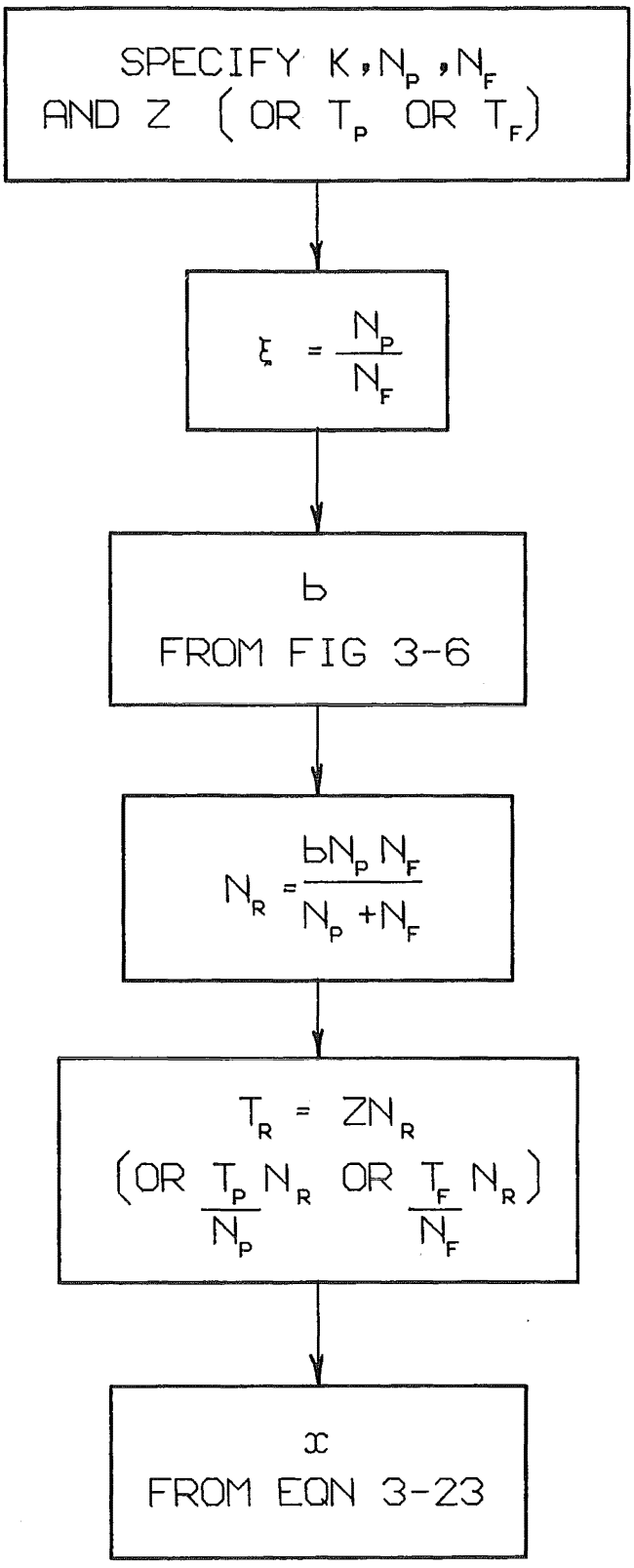


FIGURE 3-7. BREAKTHROUGH CURVE CALCULATION USING THE VHT METHOD.

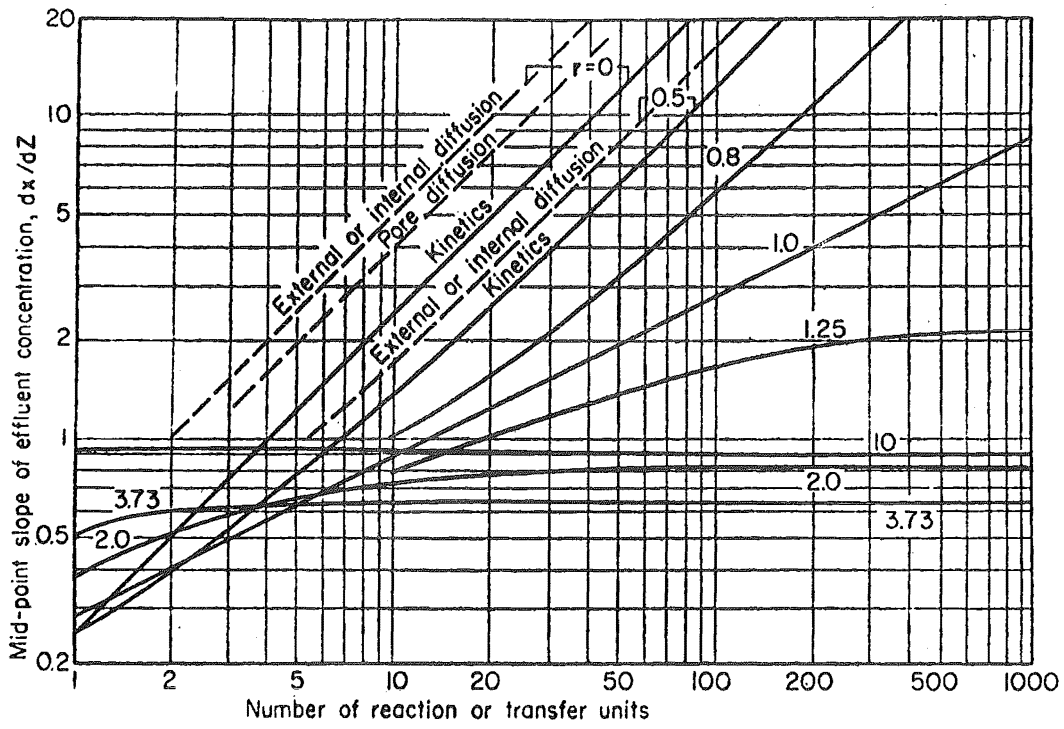


FIGURE 3-8. THE BREAKTHROUGH CURVE MID-POINT SLOPE AND THE NUMBER OF TRANSFER UNITS.

There are however some grounds for criticism of this equation. The replacement of a diffusional mechanism by a pseudo-chemical reaction is not academically satisfactory, but can be justified by its applicability, its general accuracy and the lack of a better analytical method. However, it is limited to binary systems and the effects of axial dispersion are not expressly included although modification to N_R may be suggested (Chapter 9).

Amundson (1948, 1950) using Laplace transform methods has generalised the initial and boundary conditions for several rate expressions, but not for Eqn 3-20. However this solution has been derived in Appendix 3D since it has application to non-uniform particle presaturation, and since it will describe several cycles of exhaustion and regeneration through suitable boundary conditions.

Analytical solutions involving axial dispersion are discussed in Section 9-3.

APPENDIX 3A

EVALUATION OF THE J FUNCTION

The J function can be evaluated from the integral

$$J(p,q) = 1.0 - \int_0^p \exp(-q-t) \cdot I_o(2\sqrt{qt})\,dt$$

where I_o is the modified Bessel function of order zero. The integrand is bounded and well-behaved and can be easily evaluated by numerical methods. However, the Bessel function is unbounded if evaluated separately, and will cause numerical overflow for reasonable arguments.

However, if the integrand is modified to

$$\exp[2\sqrt{qt} - (q + t)] \cdot [\exp(-2\sqrt{qt}) I_o(2\sqrt{qt})]$$

the two factors can be evaluated, both (and their product) being bounded. The factor containing the Bessel function can be evaluated using a polynomial approximation (Abramowitz and Stegun, 1965) with error less than 1.9×10^{-7}.

$$r = \frac{x}{3.75}$$

$$x < 3.75, \quad I_o(x)\exp(-x) = \sum_{i=o}^{6} a_i\, r^{2i}$$

$$3.75 < x < \infty, I_o(x)\exp(-x) = x^{-\frac{1}{2}} \left[\sum_{i=o}^{8} b_i\, r^i \right]$$

where a and b are given by:-

i	a	b
0	1.0	0.39894228
1	3.5156229	0.01328592
2	3.0899424	0.00225319
3	1.2067492	-0.00157565
4	0.2659732	0.00916281
5	0.0360768	-0.02057706
6	0.0045813	0.02635537
7	-	-0.01647633
8	-	0.00392377

The following computer program is a Fortran subroutine to calculate J.

```
0001            REAL FUNCTION JFN(P,Q)
                C
                C   PURPOSE
                C
                C     JFN CALCULATES THE VALUE OF THE J FUNCTION
                C          WITH ARGUMENTS P,Q
                C   USAGE
                C
                C        X=JFN(P,Q)
                C
                C   PARAMETERS
                C     X        VALUE OF THE J FUNCTION
                C     P,Q      ARGUMENTS
                C
                C   SUBPROGRAMS REQUIRED
                C
                C     IOEXP    LISTING FOLLOWS
                C     QSF      NUMERICAL INTEGRATION
                C
                C
                C
                C
                C     THE INTEGRATION ADAPTIVELY INCREASES N, THE
                C          NUMBER OF INTEGRATION STEPS.
                C
0002            REAL Z(16500)
0003            REAL JP
                C                                                    50000.0=SPE
                C                                                    10000.0=SPE
0004            EPS=0.0001
                C                                                  Q,P)301,6(ETIRW
0005            N=4
0006            JP=-10.0
                C
                C     LOOP FOR INCREASING N
                C
0007            DO 200 INCN=1,12
0008            N1=N+1
0009            DX=P/N
                C
                C     LOOP 201 FOR FUNCTION EVALUATION AT N+1 PIVOTAL POINTS
                C
0010            DO 201 IDO=1,N1
0011            X=(IDO-1)*DX
0012            ARG=2.0*SQRT(Q*X)
0013            CALL IOEXP(ARG,RES)
0014         17 Z(IDO)=EXP(ARG-Q-X)*RES
0015        201 CONTINUE
                C
```

```
C     INTEGRATION
C
      CALL QSF(DX,Z,Z,N1)
      JFN=1.0-Z(N1)
C                                                        NFJ,XD,N)301,6(ETIRW
  103 FORMAT(6G15.5)
C
C     IF INTEGRATION CONVERGED, BRANCH OUT OF LOOP 200
C
      EJ=JFN-JP
      IF(EJ.LT.EPS)GOTO18
      IF(ABS(JFN/EJ).GT.0.1/EPS)GOTO18
C
C     OTHERWISE RETURN WITH DOUBLED NUMBER OF STEPS
C
      N=N+N
      JP=JFN
  200 CONTINUE
C
C     INTEGRATION NOT CONVERGED
C
      WRITE(6,101)N,P,Q,JFN,EJ
  101 FORMAT(' NOT CONVERGED'5G15.5)
      STOP
C
C     INTEGRATION CONVERGED
C
   18 RETURN
      END
```

```
C        SUBROUTINE IOEXP
C                                                                      IO    50
C        PURPOSE                                                       IO    60
C            COMPUTE THE MODIFIED BESSEL FUNCTION I OF ORDER ZERO      IO    70
C                    *EXP(-X)
C
C        SOURCE
C         A MODIFICATION OF THE FUNCTION IO,IBM SCIENTIFIC SUBROUTINES
C                                                                      IO    80
C        USAGE                                                         IO    90
C            CALL IOEXP(X,RIO)
C                                                                      IO   110
C        DESCRIPTION OF PARAMETERS                                     IO   120
C            X    -GIVEN ARGUMENT OF THE BESSEL FUNCTION I OF ORDER 0 IO   130
C            RIO  -RESULTANT VALUE OF THE BESSEL FUNCTION I OF ORDER 0 IO   140
C                                                                      IO   150
C        REMARKS                                                       IO   160
C            LARGE VALUES OF THE ARGUMENT MAY CAUSE OVERFLOW IN THE    IO   170
C            BUILTIN EXP-FUNCTION                                      IO   180
C                                                                      IO   190
C        SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED                 IO   200
C           NONE                                                       IO   210
C                                                                      IO   220
C        METHOD                                                        IO   230
C           POLYNOMIAL APPROXIMATIONS GIVEN BY E.E. ALLEN ARE USED FOR IO   240
C           CALCULATION.                                               IO   250
C           FOR REFERENCE SEE                                          IO   260
C           M. ABRAMOWITZ AND I.A. STEGUN,'HANDBOOK OF MATHEMATICAL    IO   270
C           FUNCTIONS', U.S. DEPARTMENT OF COMMERCE, NATIONAL BUREAU OF IO   280
C           STANDARDS APPLIED MATHEMATICS SERIES, 1966, P.378.         IO   290
C                                                                      IO   300
C     ..................................................................IO   310
C                                                                      IO   320
0001          SUBROUTINE IOEXP(X,RIO)
0002          RIO=ABS(X)                                               IO   340
0003          IF(RIO-3.75)1,1,2                                        IO   350
0004        1 Z=X*X*7.111111E-2                                        IO   360
0005          RIO=(((((  4.5813E-3*Z+3.60768E-2)*Z+2.659732E-1)*Z+1.206749E0)*Z  IO   370
             1+3.089942E0)*Z+3.515623E0)*Z+1.                          IO   380
0006          RIO=RIO*EXP(-X)
0007          RETURN                                                   IO   390
0008        2 Z=3.75/RIO                                               IO   400
0009          RIO= 1.0/SQRT(RIO)*(((((((((3.92377E-3*Z-1.647633E-2)*Z
             1+2.635537E-2)*Z-2.057706E-2)*Z+9.16281E-3)*Z-1.57565E-3)*Z  IO   420
             2+2.25319E-3)*Z+1.328592E-2)*Z+3.989423E-1)               IO   430
0010          RETURN                                                   IO   440
0011          END                                                      IO   450
```

```
C                                                                       QSF  003
C       SUBROUTINE QSF                                                  QSF  004
C                                                                       QSF  005
C
C       SOURCE
C          IBM SCIENTIFIC SUBROUTINES PACKAGE
C
C       PURPOSE                                                         QSF  006
C          TO COMPUTE THE VECTOR OF INTEGRAL VALUES FOR A GIVEN         QSF  007
C          EQUIDISTANT TABLE OF FUNCTION VALUES.                        QSF  008
C                                                                       QSF  009
C       USAGE                                                           QSF  010
C          CALL QSF (H,Y,Z,NDIM)                                        QSF  011
C                                                                       QSF  012
C       DESCRIPTION OF PARAMETERS                                       QSF  013
C          H      - THE INCREMENT OF ARGUMENT VALUES.                   QSF  014
C          Y      - THE INPUT VECTOR OF FUNCTION VALUES.                QSF  015
C          Z      - THE RESULTING VECTOR OF INTEGRAL VALUES. Z MAY BE   QSF  016
C                   IDENTICAL WITH Y.                                   QSF  017
C          NDIM   - THE DIMENSION OF VECTORS Y AND Z.                   QSF  018
C                                                                       QSF  019
C       REMARKS                                                         QSF  020
C          NO ACTION IN CASE NDIM LESS THAN 3.                          QSF  021
C                                                                       QSF  022
C       SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED                   QSF  023
C          NONE                                                         QSF  024
C                                                                       QSF  025
C       METHOD                                                          QSF  026
C          BEGINNING WITH Z(1)=0, EVALUATION OF VECTOR Z IS DONE BY     QSF  027
C          MEANS OF SIMPSONS RULE TOGETHER WITH NEWTONS 3/8 RULE OR A   QSF  028
C          COMBINATION OF THESE TWO RULES. TRUNCATION ERROR IS OF       QSF  029
C          ORDER H**5 (I.E. FOURTH ORDER METHOD). ONLY IN CASE NDIM=3   QSF  030
C          TRUNCATION ERROR OF Z(2) IS OF ORDER H**4.                   QSF  031
C          FOR REFERENCE, SEE                                           QSF  032
C          (1) F.B.HILDEBRAND, INTRODUCTION TO NUMERICAL ANALYSIS,      QSF  033
C              MCGRAW-HILL, NEW YORK/TORONTO/LONDON, 1956, PP.71-76.    QSF  034
C          (2) R.ZURMUEHL, PRAKTISCHE MATHEMATIK FUER INGENIEURE UND    QSF  035
C              PHYSIKER, SPRINGER, BERLIN/GOETTINGEN/HEIDELBERG, 1963,  QSF  036
C              PP.214-221.                                              QSF  037
C                                                                       QSF  038
C     ..................................................................QSF  039
C                                                                       QSF  040
0001        SUBROUTINE QSF(H,Y,Z,NDIM)                                  QSF  041
C                                                                       QSF  042
C                                                                       QSF  043
0002        DIMENSION Y(1),Z(1)                                         QSF  044
C                                                                       QSF  045
0003        HT=.3333333*H                                               QSF  046
0004        IF(NDIM-5)7,8,1                                             QSF  047
```

```
                C                                                               QSF  048
                C     NDIM IS GREATER THAN 5. PREPARATIONS OF INTEGRATION LOOP   QSF  049
0005            1   SUM1=Y(2)+Y(2)                                              QSF  050
0006                SUM1=SUM1+SUM1                                              QSF  051
0007                SUM1=HT*(Y(1)+SUM1+Y(3))                                    QSF  052
0008                AUX1=Y(4)+Y(4)                                              QSF  053
0009                AUX1=AUX1+AUX1                                              QSF  054
0010                AUX1=SUM1+HT*(Y(3)+AUX1+Y(5))                               QSF  055
0011                AUX2=HT*(Y(1)+3.875*(Y(2)+Y(5))+2.625*(Y(3)+Y(4))+Y(6))     QSF  056
0012                SUM2=Y(5)+Y(5)                                              QSF  057
0013                SUM2=SUM2+SUM2                                              QSF  058
0014                SUM2=AUX2-HT*(Y(4)+SUM2+Y(6))                               QSF  059
0015                Z(1)=0.                                                     QSF  060
0016                AUX=Y(3)+Y(3)                                               QSF  061
0017                AUX=AUX+AUX                                                 QSF  062
0018                Z(2)=SUM2-HT*(Y(2)+AUX+Y(4))                                QSF  063
0019                Z(3)=SUM1                                                   QSF  064
0020                Z(4)=SUM2                                                   QSF  065
0021                IF(NDIM-6)5,5,2                                             QSF  066
                C                                                               QSF  067
                C     INTEGRATION LOOP                                          QSF  068
0022            2   DO 4 I=7,NDIM,2                                             QSF  069
0023                SUM1=AUX1                                                   QSF  070
0024                SUM2=AUX2                                                   QSF  071
0025                AUX1=Y(I-1)+Y(I-1)                                          QSF  072
0026                AUX1=AUX1+AUX1                                              QSF  073
0027                AUX1=SUM1+HT*(Y(I-2)+AUX1+Y(I))                             QSF  074
0028                Z(I-2)=SUM1                                                 QSF  075
0029                IF(I-NDIM)3,6,6                                             QSF  076
0030            3   AUX2=Y(I)+Y(I)                                              QSF  077
0031                AUX2=AUX2+AUX2                                              QSF  078
0032                AUX2=SUM2+HT*(Y(I-1)+AUX2+Y(I+1))                           QSF  079
0033            4   Z(I-1)=SUM2                                                 QSF  080
0034            5   Z(NDIM-1)=AUX1                                              QSF  081
0035                Z(NDIM)=AUX2                                                QSF  082
0036                RETURN                                                      QSF  083
0037            6   Z(NDIM-1)=SUM2                                              QSF  084
0038                Z(NDIM)=AUX1                                                QSF  085
0039                RETURN                                                      QSF  086
                C     END OF INTEGRATION LOOP                                   QSF  087
                C                                                               QSF  088
0040            7   IF(NDIM-3)12,11,8                                           QSF  089
                C                                                               QSF  090
                C     NDIM IS EQUAL TO 4 OR 5                                   QSF  091
0041            8   SUM2=1.125*HT*(Y(1)+Y(2)+Y(2)+Y(2)+Y(3)+Y(3)+Y(3)+Y(4))     QSF  092
0042                SUM1=Y(2)+Y(2)                                              QSF  093
0043                SUM1=SUM1+SUM1                                              QSF  094
0044                SUM1=HT*(Y(1)+SUM1+Y(3))                                    QSF  095
0045                Z(1)=0.                                                     QSF  096
```

```
0046                AUX1=Y(3)+Y(3)                                          QSF  097
0047                AUX1=AUX1+AUX1                                          QSF  098
0048                Z(2)=SUM2-HT*(Y(2)+AUX1+Y(4))                           QSF  099
0049                IF(NDIM-5)10,9,9                                        QSF  100
0050              9 AUX1=Y(4)+Y(4)                                          QSF  101
0051                AUX1=AUX1+AUX1                                          QSF  102
0052                Z(5)=SUM1+HT*(Y(3)+AUX1+Y(5))                           QSF  103
0053             10 Z(3)=SUM1                                               QSF  104
0054                Z(4)=SUM2                                               QSF  105
0055                RETURN                                                  QSF  106
                 C                                                          QSF  107
                 C     NDIM IS EQUAL TO 3                                   QSF  108
0056             11 SUM1=HT*(1.25*Y(1)+Y(2)+Y(2)-.25*Y(3))                  QSF  109
0057                SUM2=Y(2)+Y(2)                                          QSF  110
0058                SUM2=SUM2+SUM2                                          QSF  111
0059                Z(3)=HT*(Y(1)+SUM2+Y(3))                                QSF  112
0060                Z(1)=0.                                                 QSF  113
0061                Z(2)=SUM1                                               QSF  114
0062             12 RETURN                                                  QSF  115
0063                END                                                     QSF  116
```

APPENDIX 3B

CONSTANT PATTERN SOLUTIONS

This appendix develops the equations for ion exchange breakthrough curves under constant pattern conditions for a constant separation factor and either solution-side or particle-side control, (linear or quadratic rate expression).

The solution mass balance

$$\frac{\partial x}{\partial N} + \frac{\partial \bar{y}}{\partial T} = 0 \qquad (3B\text{-}1)$$

is a hyperbolic partial differential equation, which, with a rate equation in the form

$$\frac{\partial y}{\partial T} = F(x,y)$$

and the constant pattern condition, $x = \bar{y}$, can be solved by the method of characteristics (Lapidus and Rosen, 1954). The equations to be solved are:-

$$\begin{bmatrix} 1 & 1 \\ dN & dT \end{bmatrix} \begin{bmatrix} \partial x/\partial N \\ \partial x/\partial T \end{bmatrix} = \begin{bmatrix} 0 \\ dx \end{bmatrix}$$

There is a characteristic equation

$$T = N + \xi$$

where ξ is a constant of integration, which when satisfied reduces the partial differential equation to an ordinary differential equation, in this case $dx = 0$. The value of x along any characteristic (selected by the value of ξ) will be a constant and a function of ξ alone.

Since $F(x,x) = \frac{\partial \bar{y}}{\partial T} = \frac{\partial x}{\partial T} = \frac{\partial x}{\partial \xi}\frac{\partial \xi}{\partial T}$

and since $\partial \xi = \partial T$ at constant N, the breakthrough curve will be given by

$$\int_{x_1}^{x} \frac{dx}{F(x,x)} = \int_{\xi_1}^{\xi} d\xi \qquad (3B\text{-}2)$$

For film diffusion

$$F(x,x) = \frac{d\bar{y}}{dT} = x - x^* = x - \frac{y}{K - (K-1)y} = x - \frac{x}{K - (K-1)x}$$

and Eqn 3B-1 becomes

$$\int_{\xi_1}^{\xi} d\xi = \int_{x_1}^{x} \frac{K - (K-1)x}{x(1-x)(K-1)}\, dx$$

$$\therefore\ T - N = \left[\frac{K}{K-1}\ln x - \frac{1}{K-1}(1-x)\right] - \alpha_f$$

where α_f is an arbitrary constant, which can be evaluated from the overall mass balance, Eqn 2-27,

$$N = \int_{x=o}^{x=1} T\, dx \quad \text{where } T = N + \frac{K}{K-1}\ln x - \frac{1}{K-1}\ln(1-x) - \alpha_f$$

$$\therefore\ N = \int_{x=o}^{1} N\, dx + \frac{K}{K-1}\int_{x=o}^{1} \ln x\, dx - \frac{1}{K-1}\int_{x=o}^{1} \ln(1-x)\, dx - \int_{x=o}^{1} \alpha_f\, dx$$

The substitution of p for 1-x and standard integral tables (Weast, 1968, page A-229, Eqn 544) yields the result:-

$$\alpha_f = -1$$

The constant pattern breakthrough curve for film diffusion control is:-

$$T - N - 1 = \frac{K}{K-1}\ln x - \frac{1}{K-1}\ln(1-x) \qquad (3B\text{-}3)$$

For particle diffusion:

$$F(x,x) = \frac{d\bar{y}}{dT} = (y^* - y)$$

The analogous algebra gives

$$T - N + 1 = \frac{1}{K-1}\ln x - \frac{K}{K-1}\ln(1-x) \qquad (3B\text{-}4)$$

corresponding to $\alpha_p = 1.0$.

For the quadratic driving-force expression

$$F(x,x) = \frac{d\bar{y}}{dT} = \frac{(y^*)^2 - y}{2y}$$

including the correction factor, ψ, (Eqn 3-14) in the definition of T, a similar derivation leads to

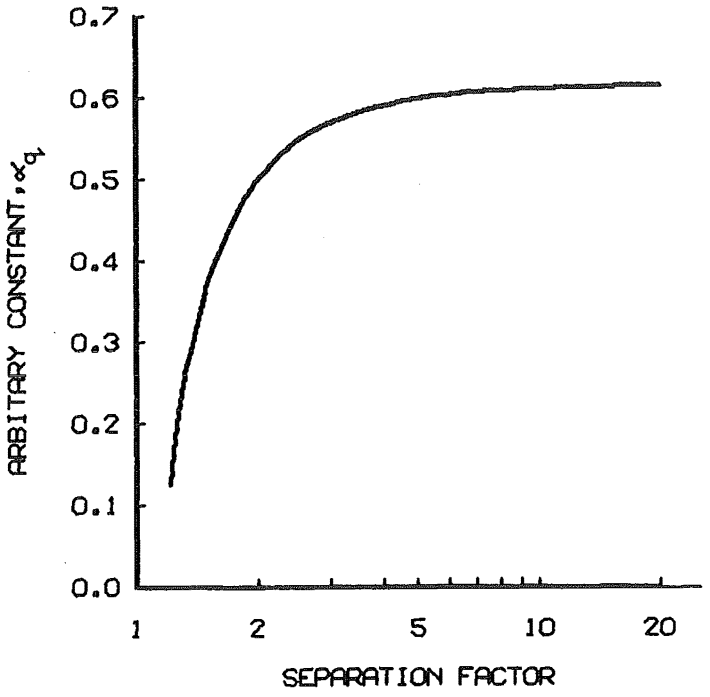
$$T - N + \alpha_q = \frac{2}{K^2 - 1} \ln x - \frac{K}{K - 1} \ln (1 - x) \frac{-K}{K + 1} \ln \left(x + \frac{K + 1}{K - 1}\right) \quad (3B\text{-}5)$$

in conflict with Vermeulen (1953) Eqn 35, but in agreement with Hall et al. (1966), Eqn 53a.

The arbitrary constant can also be analytically expressed, but is not constant for this rate expression

$$\alpha_q = 2 + \frac{K}{K - 1}\left[\ln \frac{K + 1}{K - 1} - \frac{2K}{K + 1} \ln \frac{2K}{K - 1}\right]$$

As Graph 3B-1 shows, α_q can be assumed constant for an equilibrium ratio greater than 3 with little error.



GRAPH 3B-1. THE VARIATION OF THE ARBITARY CONSTANT α_q WITH SEPARATION FACTOR.

APPENDIX 3C

PROGRAM LISTING - VHT

```
C
C                                VHT
C
C
C     BREAKTHROUGH CURVES BY VERMEULEN-HIESTER-THOMAS METHOD
C
C    PURPOSE
C
C      VHT IS A MAINLINE PROGRAM TO COMPUTE BREAKTHROUGH CURVES BY THE
C      VERMEULEN-HIESTER-THOMAS METHOD,OPTIONALLY EXTENDED TO ALLOW FOR
C      AXIAL DISPERSION
C
C    USAGE
C
C      FOR EACH DATA CARD READ BREAKTHROUGH CURVES ARE CALCULATED
C      AT 10,20,40,60,80,100 TRANSFER UNITS
C
C    INPUT DATA
C
C          READ(5,100)K,ZETA,THETA,B
C     100 FORMAT(4F10.4)
C
C    PARAMETERS
C
C      K        SEPARATION FACTOR
C      ZETA     MECHANISM PARAMETER
C      THETA    DISPERSION PARAMETER (0.0 FOR NO AXIAL DISPERSION )
C      B        CORRECTION FACTOR FOR NON-LINEAR EQUILIBRIUM
C
C      IF NO VALUE FOR B IS SUPPLIED,VHT WILL PROVIDE ONE IF A REASONABLE
C      APPROXIMATION IS POSSIBLE FOR FIGURE 3-6.IF NOT,AN ERROR MESSAGE
C      IS GIVEN AND THAT DATA CARD IGNORED
C
C    SUBPROGRAMS REQUIRED
C
C      ERF      TO CALCULATE THE ERROR FUNCTION
C      JFN      TO CALCULATE THE J FUNCTION-LISTED IN APPENDIX 3A
C      RTEFCE   LISTING FOLLOWS
C
0001            REAL NRTRK
0002            REAL JFN,NR,N,K
0003            DIMENSION V(19)
0004            DIMENSION ZV(20)
0005            DATA ZV/.2,.4,.6,.7,.8,.85,.9,.95,1.,1.05,1.1,1.15,1.2,1.3,1.4,
               11.6,1.8,2.0,0.0,0.0/
0006            RTPI=1.77245
0007            V(1)=10.0
0008            V(2)=20.0
0009            V(3)=40.
```

```
0010              V(4)=60.
0011              V(5)=80.
0012              V(6)=100.0
0013              INT=6
0014              CF=1.3
0015            1 READ(5,100)K,ZETA,THETA,B
0016          100 FORMAT(4F10.4)
                C
                C     CALCULATE B UNLESS SUPPLIED
                C
0017              IF(B.GT.0.000001)GOTO3
0018              IF(K.LE.4.0.AND.K.GE.0.9)GOTO10
0019              IF(K.LE.0.91.AND.K.GE.0.2)GOTO11
0020              IF(ZETA.GE.-5.0.AND.ZETA.LE.0.01)GOTO10
0021              IF(K.LE.0.2.AND.ZETA.LT.0.4.AND.ZETA.GT.-0.1)GOTO10
0022              IF(ZETA.LE.-5.0.AND.K.LE.0.2)GOTO12
0023              WRITE(6,110)ZETA,K,THETA
0024          110 FORMAT('0ZETA 'G15.5,10X'K'G15.5,10X'THETA'G15.5'NO B VALUE AVAILA
                   1BLE')
0025              GOTO1
0026           10 B=2.0*K/(1.0+K)
0027              GOTO3
0028           11 BM=2.0*K/(1.0+K)
0029              BP=(1.0+K)/2.0
0030              PHI=(ZETA-1.0)/(ZETA+1.0)
0031              IF(ZETA.LT.-5.0)PHI=1.0
0032              B=((1.0+PHI)*BP+(1.0-PHI)*BM)/2.0
0033              GOTO3
0034           12 B=(K+1.0)/2.0
                C
                C     LOOP 201 FOR EACH N VALUE
                C
0035            3 DO201IN=1,INT
0036              N=V(IN)
                C
                C     CALCULATE NR, NUMBER OF REACTION TRANSFER UNITS
                C
0037              G=1.+ZETA
0038              IF(ZETA.GT.1.0)G=1.0+1.0/ZETA
0039              IF(ZETA.LT.-5.0)G=1.0
0040              VN=G/B+CF*THETA
0041              NR=N/VN
0042              WRITE(6,101)ZETA,K,THETA,N,NR,B
0043          101 FORMAT('0'T7'ZETA'T23'K'T54'N'T68'NR'T83'B'T35'THETA'/6G15.5//
                   1' 'T9'Z'T24'X'T40'T'T55'TR')
                C
                C     LOOP 200 FOR BREAKTHROUGH CURVE POINTS
                C
0044              DO 200 IZ=1,18
```

```
0045                Z=ZV(IZ)
0046                TR=Z*NR
0047                T=Z*N
0048                NRTRK=NR*TR/K
0049                IF(NRTRK.LT.40.0) GO TO 20
                C
                C       USE ONSAGER ASYMPTOTIC EXPANSION
                C
0050                SNR=SQRT(NR)
0051                STR=SQRT(TR)
0052                SNRK=SQRT(NR/K)
0053                STRK=SQRT(TR/K)
0054                SNRTRK=SQRT(SQRT(NRTRK))
0055                A=STRK-SNR
0056                IF(A.GT.1.0)GOTO23
0057                H1=ERF(STRK-SNR)
0058                T1=RTPI*(1.0-H1)*EXP(A*A)
0059             22 T1=T1-1.0/(STRK+SNRTRK)
0060                A=SNRK-STR
0061                IF(A.GT.1.0)GOTO25
0062                H2=ERF(SNRK-STR)
0063                T2=RTPI*(1.0-H2)*EXP(A*A)
0064             24 T2=T2+1.0/(STR+SNRTRK)
0065                X=1.0+T1/T2
0066                X=1.0/X
0067                WRITE(6,103)Z,X,T,TR,H1,H2,T1,T2
0068            103 FORMAT(' *' 8G15.5)
0069                GO TO 200
0070             23 T1=RTEFCE(A)
0071                GOTO22
0072             25 T2=RTEFCE(A)
0073                GOTO24
                C
                C       USE J FUNCTION
                C
0074             20 U=(1.0-K)/K*(TR-NR)
0075                A=JFN(NR/K,TR)
0076                C=EXP(U)
0077                D=JFN(NR,TR/K)
0078                E=C-C*D
0079                X=A/(A+E)
0080                WRITE(6,102)Z,X,T,TR,U,A,E,C,D
0081            102 FORMAT(9G14.5)
0082            200 CONTINUE
0083            201 CONTINUE
0084                GO TO 1
0085                END
```

```
0001              FUNCTION ERF(XD)
                  C
                  C   PURPOSE
                  C
                  C     THIS PROGRAM COMPUTES THE ERROR FUNCTION FOR ANY ARGUMENT XD
                  C     USING EQN 7.1.26 ABRAHAMOWITZ AND STEGUN
                  C
                  C     THE MAXIMUM ERROR IS LESS THAN 1.5 E-7
                  C
0002              DATA P/0.3275911/
0003              DATA A1,      A2,      A3,      A4,      A5      /
                 10.254829592,-0.284496736,1.421413741,-1.4531572027,1.061405429/
0004              X=XD
0005              S=1.0
0006              IF(X.LT.0.0)S=-1.0
0007              ERF=S
0008              IF(X.GT.5.0)RETURN
0009              X=ABS(X)
0010              T=1.0/(1.0+P*X)
0011              F=((((A5*T+A4)*T+A3)*T+A2)*T+A1)*T*EXP(-X*X)
0012              ERF=S*(1.0-F)
0013              RETURN
0014              END
```

```
0001              FUNCTION RTEFCE(A)
                  C
                  C   PURPOSE
                  C
                  C     THIS FUNCTION EVALUATES
                  C         RTEFCE(A)=SQRT(PI)*ERFC(A)*EXP(A*A)
                  C                  =(1+S)/A
                  C      WHERE 1+S IS THE SERIES SUMMED HEREIN.
                  C
                  C     SEE ABRAHAMOWITZ AND STEGUN EQN 7-1-23
                  C
                  C
0002              LOGICAL DEBUG/.TRUE./
0003              DEBUG=.FALSE.
0004              SP1=1.0
0005              T=1.0
0006              DO200I=1,50
0007              F=-(I+I-1)/2.0/A/A
0008              T=T*F
0009              SP1=SP1+T
0010              IF(DEBUG)WRITE(6,101)A,I,F,T,SP1
0011            101 FORMAT(6G15.5)
0012              IF(I.LT.5)GOTO200
0013              IF(T/SP1.LT.0.00001)GOTO3
0014            200 CONTINUE
0015              WRITE(6,100)A,F,T,SP1
0016            100 FORMAT(' POSSIBLE ERROR IN RTEFCE**********'4G15.5)
0017              3 RTEFCE=SP1/A
0018              RETURN
0019              END
```

APPENDIX 3D

THE EXTENSION OF THOMAS' ANALYTICAL SOLUTION TO ARBITRARY INITIAL OR BOUNDARY CONDITIONS

3D-1 The Differential Equations

The equations to be solved are:-

The solution mass balance $\frac{\partial x}{\partial N} + \frac{\partial Y}{\partial T} = 0$ (3D-1)

(Eqn 3-1)

The rate equation $\frac{\partial Y}{\partial T} = x(1 - y) - \frac{Y}{K}(1 - x)$ (3D-2)

(Eqn 3-20)

Equation 3D-1 is the necessary and sufficient condition for the existence of a function f(N,T) with an exact differential

$$df = y\,dN - x\,dT$$

In addition, $df = \frac{\partial f}{\partial N}\,dN + \frac{\partial f}{\partial T}\,dT$

$\therefore\ y = \frac{\partial f}{\partial N}$, $x = -\frac{\partial f}{\partial T}$ and $\frac{\partial x}{\partial N} = -\frac{\partial^2 f}{\partial N.\partial T} = -\frac{\partial y}{\partial T}$

Substituting into the rate equation:-

$$\frac{\partial^2 f}{\partial N.\partial T} + \frac{\partial f}{\partial T} + \frac{1}{K} \cdot \frac{\partial f}{\partial N} + \left(\frac{1 - K}{K}\right)\left(\frac{\partial f}{\partial N}\right)\left(\frac{\partial f}{\partial T}\right) = 0 \qquad (3D\text{-}3)$$

This equation can be linearised by using a form of the Thomas transformation (Eqn 3-22) in terms of a function, $\phi(N,T)$

$$f(N,T) = \frac{K}{1 - K} \ln\left[\phi(N,T) \cdot \exp\left(-N - \frac{T}{K}\right)\right]$$

The required differentials are:-

$$\frac{\partial f}{\partial N} = \frac{K}{1 - K}\left(\frac{1}{\phi}\frac{\partial \phi}{\partial N} - 1\right)$$

$$\frac{\partial f}{\partial T} = \frac{K}{1 - K}\left(\frac{1}{\phi}\frac{\partial \phi}{\partial T} - \frac{1}{K}\right)$$

$$\frac{\partial^2 f}{\partial N.\partial T} = \frac{K}{1 - K} \cdot \frac{1}{\phi} \cdot \left(\frac{\partial^2 \phi}{\partial N.\partial T} - \frac{1}{\phi} \cdot \frac{\partial \phi}{\partial N} \cdot \frac{\partial \phi}{\partial T}\right)$$

These can be substituted into Eqn 3D-3 to give

$$\frac{\partial^2 \phi}{\partial N \partial T} - \frac{\phi}{K} = 0 \qquad (3D\text{-}4)$$

3D-2 Boundary Conditions

The boundary condition is specified at the top of the bed (N = 0)

where the solution concentration history is

$$x = x_o(T) = \frac{-\partial f}{\partial T} = \frac{K}{K - 1}\left(\frac{1}{\phi}\frac{\partial \phi}{\partial T} - \frac{1}{K}\right)$$

This is an ordinary differential equation

$$\frac{1}{\phi}\frac{d\phi}{dT} = \left(\frac{K - 1}{K}\right) x_o(T) + \frac{1}{K}$$

which must be solved from T = 0 to some T from

$$\int_{\phi=1.0}^{\phi} \frac{d\phi}{\phi} = \int_{T=0}^{T} \left[\left(\frac{K - 1}{K}\right) x_o(T) + \frac{1}{K}\right] dT$$

The lower limit of the integral at T = 0 (and also at N = 0 for the boundary condition), $\phi(0,0)$, is normalised to 1.0, as it does not affect either x or y.

Integrating

$$\phi(0,T) = \exp\left[\frac{T + (K - 1)I_x}{K}\right] = G(T) \qquad (3D\text{-}5)$$

where $I_x(T) = \int_o^T x_o(\tau)\,d\tau$.

3D-3 The Initial Condition

The initial condition arises from the state of the resin in the bed at T = 0. The resin concentration profile is

$$y = y_o(N) = \frac{\partial f}{\partial N} = \frac{K}{1 - K}\left(\frac{1}{\phi}\frac{\partial \phi}{\partial N} - 1\right)$$

This is also an ordinary differential equation and can be solved as in the previous section

$$\phi(N,0) = \exp\left[N + \frac{1 - K}{K} I_y\right] = F(N) \qquad (3D\text{-}6)$$

where

$$I_y(N) = \int_o^N y_o(\mu)\,d\mu.$$

3D-4 Method of Solution

The equation 3D-4 can be solved with conditions 3D-5 and 3D-6 using the same method as Schumann (1929). Two sets of equations are used; one with simple initial conditions and the other with simple boundary conditions:-

$$\frac{\partial^2 u}{\partial N . \partial T} - \frac{u}{K} = 0 \quad \text{with } u(0,T) = G(T) \text{ for } N = 0$$
$$\text{and } u(N,0) = 1 \text{ for } T = 0 \qquad (3D\text{-}4\,a)$$

$$\frac{\partial^2 v}{\partial N . \partial T} - \frac{v}{K} = 0 \quad \text{with } v(0,T) = 0 \text{ for } N = 0$$
$$\text{and } v(N,0) = F(N) - 1 \text{ for } T = 0 \qquad (3D\text{-}4\,b)$$

The sum u + v satisfies the equations 3D-4, 3D-5, 3D-6.

For the set of equations in u, the Laplace transformation is taken with respect to T (using p = L{T}) giving

$$p\frac{d\bar{u}}{dN} - \frac{\bar{u}}{K} = 0 \qquad (3D\text{-}7)$$

since $\left.\frac{du}{dN}\right|_{T=0} = 0$ because u(N,0) = 1 for T = 0.

This ordinary differential equation in $\bar{u}$ with respect to N has an initial condition $\bar{u} = \bar{G}(p)$ at N = 0 and can be integrated to:-

$$\bar{u} = \bar{G}(p)\exp\left(\frac{N}{pK}\right) \qquad (3D\text{-}8)$$

In the same way for the v group of equations, taking Laplace transforms with respect to N (q = L{N}) and integrating the resultant equation

$$\bar{v} = \left(\bar{F}(q) - \frac{1}{q}\right)\exp\left(\frac{T}{qK}\right) \qquad (3D\text{-}9)$$

These Laplace transforms can be inverted

$$\bar{u} = L^{-1}\left\{p\bar{G}(p) \cdot \frac{\exp\left(\frac{N}{pK}\right)}{p}\right\}$$

$$= L^{-1}\left\{\left[p\bar{G}(p) - 1\right]\frac{\exp\left(\frac{N}{pK}\right)}{p} + \frac{\exp\left(\frac{N}{pK}\right)}{p}\right\} \qquad (3D\text{-}10)$$

Since $L\{G'(T)\} = p\bar{G}(p) - G(o)$ and $G(o) = \phi(o,o) = 1.0$

then $L\{G'(T)\} = p\bar{G}(p) - 1$

The inverse of the first term in Eqn 3D-10 can be found by convolution and the second is a standard form

$$u = I_o(2\sqrt{\frac{NT}{K}}) + \int_o^T G'(\tau) \cdot I_o\left[2\sqrt{\frac{N(T-\tau)}{K}}\right] d\tau$$

and similarly

$$v = \int_o^N F'(\mu) I_o\left[2\sqrt{\frac{T(N-\mu)}{K}}\right] d\mu$$

The function ϕ can be obtained from the sum

$$\phi(N,T) = u + v = I_o(2\sqrt{\frac{NT}{K}}) + \int_o^T G(\tau) \cdot I_o\left[2\sqrt{\frac{N(T-\tau)}{K}}\right] d\tau$$

$$+ \int_o^N F'(\mu) \cdot I_o\left[2\sqrt{\frac{T(N-\mu)}{K}}\right] d\mu \qquad (3D\text{-}11)$$

The required derivatives of F and G are obtainable from

$$F'(N) = \left[1 + \frac{1-K}{K} y_o(N)\right] \cdot \exp\left[N + \frac{1-K}{K} I_y\right] \qquad (3D\text{-}12)$$

$$G'(T) = \left[1 + \frac{(K-1)}{K} x_o(T)\right] \cdot \exp\left[\frac{T + (k-1) I_x}{K}\right] \qquad (3D\text{-}13)$$

The values of x and y result from differentiation of the function ϕ

$$x = -\frac{\partial f}{\partial T} = \frac{K}{K-1}\left(\frac{1}{\phi}\frac{\partial \phi}{\partial T} - \frac{1}{K}\right) \qquad (3D\text{-}14)$$

$$y = \frac{\partial f}{\partial N} = \frac{K}{1-K}\left(\frac{1}{\phi}\frac{\partial \phi}{\partial N} - 1\right) \qquad (3D\text{-}15)$$

These equations can provide breakthrough curves or column profiles if $x_o(T)$ or $y_o(N)$ are specified.

Chapter 10 discusses the particular concentration history of repeated cycles of $x_o = 1.0$ exhaustion and $x_o = 0.0$ (regeneration) with an arbitrary resin concentration profile $y_o(N)$.

D-5. Reduction to Thomas's Solution

Equation 3D-11 will reduce to the result derived by Thomas for the conditions:-

$$x_o(T) = 1.0$$

$$y_o(N) = 0.0$$

$I_x = T$, $\qquad I_y = 0$

$F'(N) = \exp(N)$ $\qquad G'(T) = \exp(T)$

$$\therefore \quad \phi(N,T) = I_o(2\sqrt{\frac{NT}{K}} + \int_o^T \exp(\tau) \cdot I_o\left[2\sqrt{\frac{N(T-\tau)}{K}}\right] d\tau$$

$$+ \int_o^N \exp(\mu) \cdot I_o\left[2\sqrt{\frac{T(N-\mu)}{K}}\right] d\mu$$

By change of variable, both the definite integrals can be expressed in the form of Onsager's integral (Thomas, 1944):-

$$\psi(u,v) = e^u \int_o^u e^{-t} I_o(2\sqrt{vt})\, dt$$

and

$$\phi(N,T) = I_o(2\sqrt{\frac{NT}{K}}) + \psi(T,\frac{N}{K}) + \psi(N,\frac{T}{K})$$

which is the form derived by Thomas (Eqn 16', 1944).

CHAPTER 4

COMPUTER SOLUTION OF FIXED-BED ION EXCHANGE EQUATIONS

This chapter reviews computer methods of solution for the fixed-bed ion exchange equations.

Generally, the computer methods escape the mathematical difficulties of solving the differential equations of the various models (and allow more complex models) with one of three approaches:-

(a) sectioning the bed into "mixer-settler" equilibrium elements

(b) forming the equations into an integro-differential equation, and solving this numerically

(c) replacing the differential equations with finite-difference approximations to give algebraic equations which can be solved either in parallel by a matrix method or serially by a marching technique.

This grouping ignores, as does the literature, the use of analog computers for solving differential equations of the form produced by this problem.

The advantages of computer solutions can too easily hide their disadvantages. Computer solutions are more expensive, both for direct computer charges, and in the costs of development, verification and documentation of the program. Efficient numerical methods are needed to reduce computer time. These are now emerging, as is experience in their application to chemical engineering problems, including ion exchange, and this is helping to reduce the time and experimentation in program development.

Even when trustworthy computer programs are available, less rigorous analytical breakthrough curve equations are useful for preliminary calculations, or for immediate estimates if there is some delay in the return of computer results. In addition, the inherent assumptions of an approximate analytical solution are more apparent than those of a computer method, particularly if the verification of the computer method has not been thorough.

Many computer programs are used iteratively at the cost of increased computer time because the most convenient calculation method proceeds from unknown values to known, for example, most multicomponent distillation programs calculate column compositions when the designer is interest-

ed in the number of plates. This, and the problem of interpolation, suggests that any computer solution, particularly for the ion exchange problem, should be used to generate results in the form of tables or graphs sufficiently general and easy to use that return to the computer should be rare.

4-1. Digital Solutions - Finite Difference Methods

The solution of fixed-bed ion exchange and adsorption equations has developed with numerical methods and with computing equipment. Rose et al. (1951) used an IBM card programmed calculator to solve the equations derived by assuming equilibrium in sections of the bed. For each sequential step down the column (convergence was obtained at steps of 0.1 gram of resin), 390 punched cards were fed through the machine. Good reproduction of experimental results was achieved for the separation of benzene-hexane on silica-gel in a 0.8 cm diameter column.

Acrivos (1956) recognised that the fixed-bed adsorption process with linear rate expressions gives rise to first-order quasi-linear hyperbolic partial derivative equations, which can be readily solved using the method of characteristics (Goodwin, 1961). The advantage of the method is that the equations can be reduced to ordinary differential equations in certain directions (or characteristics) which can be solved by finite-difference methods.

Dranoff and Lapidus (1958, 1961) extended the work using the second-order-reaction-kinetic expression (Eqn 3-20), corresponding to Thomas' analytical result (Eqn 3-23), but including multicomponent operation.

Details of the method of characteristics are found in Chapter 5, where it is applied to the fixed-bed problem as above but using linear rate expressions for film and particle diffusion to solve the model IXLR.

In a series of papers, Carter (1966, 1968, 1968, 1969) has studied isothermal and adiabatic adsorption in fixed beds using a Freundlich equilibrium isotherm with temperature dependent coefficients. The model used included fickian particle diffusion and film diffusion but not axial dispersion effects. The method of solution was to use finite differences for the derivatives in the resin radial distance, and to

solve the resulting particle differential equations in N and T (both film-side basis) by iteration, until convergence in x, y*, and y and temperatures. Notwithstanding the lack of sophistication in the numerical method and the difficulty of establishing the equilibrium relationship, remarkable agreement with experimental results was achieved, both for industrial and laboratory adsorption drying columns.

McGreavy et al. (1967) considered several numerical methods for solution of the fixed-bed adsorption equations, pointing out that appropriate numerical techniques are not well established, particularly with respect to criteria for selecting finite-difference step sizes for convergence and stability, and especially for non-linear equations.

The model used by McGreavy is similar to IXM (Chapter 7). Our models differ in that McGreavy's equations are always expressed in terms of the particle-side basis (a problem with film-side control) and that the differential form of the particle mass balance (Eqn 2-13) is used, rather than the integrated form (Eqn 2-12). McGreavy in fact attributes the stability problems experienced to this derivative form. Long computing times resulted from the small step-sizes required for stability and from the need to iterate for y*, with each iteration requiring an inversion of a 20 x 20 or 40 x 40 matrix.

However, McGreavy clearly distinguishes between the hyperbolic equations describing continuity and mass transfer in the solution and the parabolic equation in the resin. The Crank-Nicholson method was shown by trial to be superior to the Runge-Kutta method (Goodwin, 1961, page 114) or to a method developed for linear systems (Leung and Quon, 1965). The method of characteristics was tested against a direct finite-difference scheme and found superior, confirming Lapidus (1962). These results are independently confirmed in this thesis.

Morton and Murrill (1967) use a similar model and equations (except for an initial condition generalised slightly to the upflow of a binary liquid through an initially empty column and the use of the film-side basis) with an arbitrary equilibrium isotherm, directed principally toward the fractionation adsorption of binary liquid mixtures. Their method of solution uses an implicit finite difference

scheme for the parabolic partial differential equation and interation at each point. Computing speeds are poor, requiring 20 minutes to 8 hours on an IBM 7040 for columns of only 0.52 to 26 transfer units, reflecting the iterative nature of their calculation scheme (10-30 cycles were required at the optimum convergence factor) and the failure to divide the equations into hyperbolic and parabolic types, linked through the interface condition.

4-2. Digital Solutions - Integrodifferential Equation Methods.

The finite-difference methods of the previous section use numerical methods directly on the derived equations. Considerable simplification of the equations or their method of solution may be possible by using analytical methods before resorting to some numerical technique; the use of the method of characteristics in the solution of the hyperbolic partial differential equations describing fixed-bed adsorption is an example. For any problem, there is an optimum point to apply numerical methods.

Tien and Thodos (1959) followed Rosen's development for the fixed-bed ion exchange process but evaded the assumption of linear equilibrium by introducing a Freundlich equilibrium isotherm

$$y = bx^a$$

where a and b are constants. The price of this generalisation is that the solution of the integrodifferential equation

$$\frac{dx}{dN} = -\frac{24D_p}{d_p} \cdot \sum_{n=1}^{\infty} \int_0^T ab \left[x + \frac{\partial x}{\partial N}\right]^{a-1} \cdot \left[\frac{\partial x}{\partial \lambda} + \frac{\partial^2 x}{\partial \lambda \partial N}\right] \cdot$$

$$\exp\{- D_p \left(\frac{2n\pi}{d_p}\right)^2 (T - \lambda)\} \cdot d\lambda \qquad (4\text{-}1)$$

must be obtained numerically for other than the linear case, a = 1,

where d_p particle diameter (L)

D_p resin diffusivity $\left(\frac{L^2}{T}\right)$

Limitations, both in computer storage and time, restricted the generated solutions to columns of less than 23 particle phase transfer units.

Dranoff, in a series of papers summarised in Colwell and Dranoff, (1971), has studied the adsorption of organic solutes in packed beds of ion exchange resin. A computer simulation of the process was developed (Colwell, 1967; Colwell and Dranoff, 1969) to include particle diffusion, axial dispersion and non-linear equilibrium which numerically solved an equation of the same form as Eqn 4-1. The program was most successful in the absence of axial dispersion. It would seem that the application of numerical methods to the basic equations rather than the integrodifferential equation will lead to a less difficult computational problem, at least for significant axial dispersion.

4-3. Particular Fixed-Bed Models

Computer methods have been used to solve the equations of less general models for particular applications or to save computer time.

A computer simulation has been used by Chen et al. (1968) to aid scale-up prediction for an unspecified fixed-bed adsorption process. The simple model, solved using the method of characteristics, included a Freundlich isotherm and only film resistance, but provided good expression of 2, 24 and 40 inch diameter columns, even in the face of evidence that the rate was pore-diffusion controlled.

Handley and Heggs (1969) have used a numerical method to solve the Schumann model including the effect of longitudinal thermal conduction through the solid. Computational experiment has defined the areas in which this mode of heat transfer is significant. The analogous ion exchange effect is not significant.

Lee and Weber (1969) have studied the isothermal adsorption of a gas on a porous solid. Their model is interesting in that it assumes pore and film diffusion, and an arbitrary isotherm expressed as a fourth-order polynomial. Correction is made for axial variation in velocity. The solution method relies on the method of characteristics and an explicit finite-difference scheme for the pore diffusion rate equation. The explicit formulation would normally impose severe restriction on the time step size from a stability criterion of the form

$$\frac{\Delta T}{(\Delta R)^2} < \tfrac{1}{2} \quad \text{(Goodwin, 1961, p. 115).}$$

Surprisingly, Lee and Weber found the step-size associated with the hyperbolic equations more restrictive.

Similar equations to the model IXM were derived by Wheeler and Middleman (1970) for solute movement in active metabolising tissue, but included an extra term for adsorbent reacting chemically in the resin. The equations were expressed using finite difference methods as a set of about 100 ordinary differential equations. These were solved by a package program, CSMP (IBM, 1969) for digital computer similation using analogue computer methods. The ease of using CSMP was appreciated, even at the expense of increased computer time.

4-4. Analogue and Hybrid Solution Methods.

If the fixed-bed ion exchange equations can be reduced to a set of ordinary differential equations (generally by finite-difference approximations) then an analogue computer will provide uniquely fast solutions. However, as the number of equations increases, so does the required equipment complement of the computer. This quickly becomes a significant constraint, notwithstanding the larger step-sizes which can be taken in an analogue implementation of the finite-difference method, in comparison with step-sizes in a digital solution (Hanauer, 1967).

Since in the set of ordinary differential equations most will be the same form, the analogue solution of one can be used repetitively to solve all, if there is some method of storing the solution of one equation to be used as an input to the next. If a hybrid computer is available, a fast and convenient solution can be developed.

Other analogue storage methods have been devised. McGreavy (1967) refers to analogue techniques unfavourably. No detail is supplied, but it appears a mechanical curve tracer and follower was used. The results obtained were shown to compare well with digital computer solutions and with Schuman's results (apart from those for very shallow beds, for which Schuman's results are apparently incorrect).

Eteson and Zwiebel (1969) have prepared a hybrid simulation of the simple fixed-bed adsorption process with linear equilibrium and a linear rate expression. Computed results agreed well with Thomas' J function. A speed advantage of about 5 to 1 was demonstrated over a digital computer simulation run on an IBM 360/40 computer.

CHAPTER 5

THE LINEAR PARTICLE DIFFUSION MODEL (IXLR) - DIGITAL COMPUTER SOLUTION

This chapter describes the model IXLR, and its solution using numerical and digital computer methods. The method of solution is verified against analytical methods where possible to check that the equations are correctly solved. Computed results are compared with experimental data and agree well if provision is made for the separation factor to vary with concentration.

5-1 The Equations of IXLR

The equations of the model are given in Table 5-1 with the nomenclature used. Mass transfer resistance is included in either or both the resin and solution phases but the resin mass transfer rate expression is the linearised form (Eqn 2-25b).

The equilibrium expression is the normal non-linear, ion exchange form (Eqn 2-4) with the separation factor initially considered constant.

The numerical solution of these equations uses the method of characteristics (Acrivos, 1956; Dranoff and Lapidus, 1958, 1961) but differs from previous work in that the reaction-kinetic rate expression (Eqn 3-20) is not used. Application of this method reduces either formulation of the equations in Table 5-1 to a pair of ordinary differential equations (Appendix 5A) to be solved in defined directions, or characteristics (Fig. 5-1).

For T constant $$\frac{dx}{dN} = -R \qquad (5\text{-}1)$$

For N constant $$\frac{dy}{dT} = R \qquad (5\text{-}2)$$

where R, the rate expression is (Eqns 2-24, 2-25b)

$$R = \sigma(y^* - y) = \rho(x - x^*) \qquad (5\text{-}3)$$

The values of σ and ρ depend on the mechanism parameter, and are given in Table 2-1.

5-2 Initial and Boundary Conditions

IXLR solves these equations subject to initial conditions

Equation	Physical form	Generalised form
Solution mass balance, Eqn 2-11	$\frac{\partial x}{\partial t} + \frac{Q}{\varepsilon C_o}\frac{\partial y}{\partial t} + \frac{v}{\varepsilon}\frac{\partial x}{\partial z} = 0$	$\frac{\partial x}{\partial N} + \frac{\partial y}{\partial T} = 0$
Solution rate, Eqn 2-8	$\frac{\partial y}{\partial t} = k_f(x - x^*)$	$\frac{\partial y}{\partial T} = \rho(x - x^*)$
Particle rate, Eqn 2-7	$\frac{\partial y}{\partial t} = k_p(y^* - y)$	$\frac{\partial y}{\partial T} = \sigma(y^* - y)$
Surface equilibrium, Eqn 2-4	$\frac{y^*}{1 - y^*} = K\frac{x^*}{1 - x^*}$	$\frac{y^*}{1 - y^*} = K\frac{x^*}{1 - x^*}$

C_o Total solution concentration, equivalents/litre.

k Mass transfer coefficient; particle phase, k_p, or solution phase, k_f (T^{-1})

K Separation factor.

N Number of transfer units, $N = \frac{Q\,k\,z}{C_o\,v}$;

particle phase, N_p, or solution phase, N_f.

Q Resin capacity, equivalents/litre of packed column.

t Time, measured from application of feed solution to column (T).

T Characteristic time; particle phase ($T_p = ZN_p$)

or solution phase ($T_f = Z\,N_f$).

v Solution superficial velocity (LT^{-1}).

x,y Solution, particle concentration ratios.

z Distance down packed bed (L).

Z Throughput ratio, $Z = \frac{C_o\,v}{Q\,z}(t - \frac{\varepsilon z}{v})$.

ε Voidage.

ρ,σ Parameters in generalised equations, as in Table 2-1.

TABLE 5-1 . Equations and nomenclature for the digital computer model, IXLR.

corresponding to a column free of solute (y = 0 for all N at T = 0) and to boundary conditions for a constant feed composition (x = 1.0 at N = 0 for all T > 0). More general conditions are considered in Chapter 10.

However, for these particular conditions, an analytical solution is possible for x along T = 0. Since y = y* = 0 and since also x* = 0, (in equilibrium with y*), Equations 5-1 and 5-3 become

$$\frac{dx}{dN} = -R = -\rho x$$

Solving,

$$x = \exp(-\rho N) \qquad (5\text{-}4)$$

for the initial condition x = 1.0 at N = 0.

No similar analytical solution is available along N = 0 because the non-linear equilibrium expression is not in that case avoided.

5-3 Numerical Method of Solution

If a rectangular finite-difference grid corresponding to the characteristics (Fig. 5-1) is placed on the independent variable plane, a numerical solution can be formulated to provide:-

(a) a breakthrough curve (or isoplane, Sillén, 1946), given by values of the dependent variables (particularly the solution concentration, x) at the grid intersections at the bottom of the column (N = N').

(b) a column concentration profile (or isochrone) in either solution or resin concentration at some time (T = T').

The dependent variables at any point depend on the values along the characteristics through that point. These values in turn depend on all values included by these characteristics and the N = 0, T = 0 axes. A numerical method therefore must systematically calculate the concentration values at all grid intersections in the independent variable plane up to some N = N' and some T = T'.

Concentrations $x_{i,j}$ and $y_{i,j}$ at some point N = $i\Delta N$, T = $j\Delta T$ where ΔN and ΔT are the mesh spacing (Fig. 5-3) are calculated by solving the differential equations $\frac{dx}{dN} = -R$ and $\frac{dy}{dT} = R$ along the appropriate characteristics.

Many methods exist for numerical solution of ordinary differential equations. Any Runge-Kutta method (Lapidus, 1962, page 89) is unsuit-

SOLUTION OF $\frac{\partial x}{\partial N} + \frac{\partial y}{\partial T} = 0$

$$\frac{\partial y}{\partial T} = R$$

$$R = \rho(x - x^*) = \sigma(y^* - y)$$

$$\frac{y^*}{1-y^*} = K \frac{x^*}{1-x^*}$$

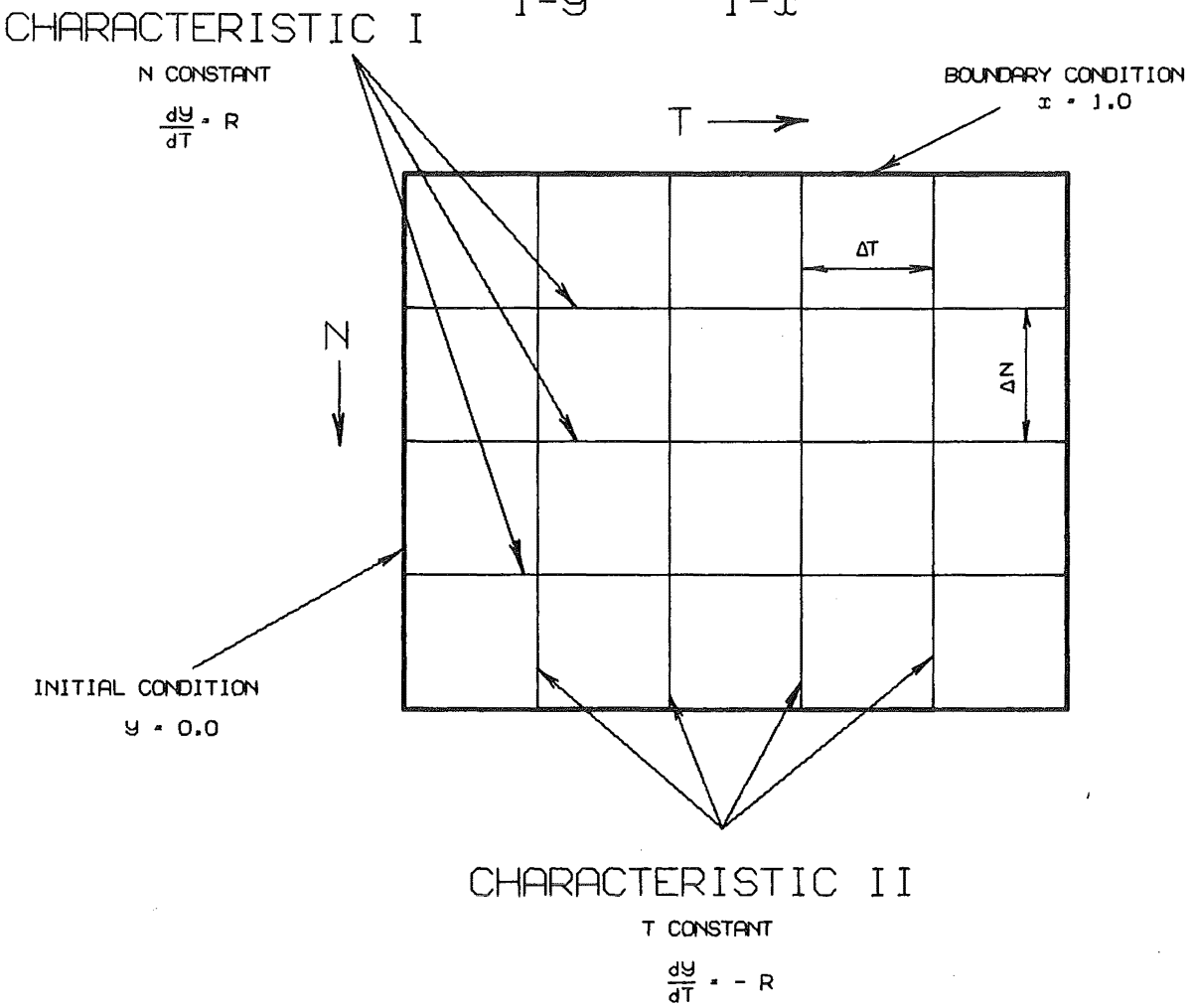


FIGURE 5-1. CHARACTERISTICS OF THE FIXED BED EQUATIONS.

able (except along N = 0 or T = 0) because it requires evaluation of derivatives between grid points. Multi-step methods require special starting procedures which complicate programming and also require more variables to be stored. Heun's method (Lapidus, 1962, page 88) is a second-order method, sometimes called the modified Euler method, which has been used throughout this work after a few trials had shown it to be superior to Euler's first-order method and to an iterative third-order method (Wilf, 1957).

Heun's method solves

$$\frac{dy}{dt} = f(y,t), \quad y_{t=0} = y_o$$

at an unknown point, $t = (n + 1)h$, from a known point, $t = n.h$, where h is the finite-difference mesh size, thus:-

$$y'_{n+1} = y_n + h\, f(y_n, t_n)$$

$$y''_{n+1} = y_n + h\, f(y'_{n+1}, t_{n+1})$$

$$y_{n+1} = \frac{y'_{n+1} + y''_{n+1}}{2} + O(h^3) \qquad (5\text{-}5)$$

The calculation scheme used modifies this method slightly, solving a pair of equations perpendicular to each other. Figures 5-2 and 5-3 detail the sequence for calculating x_{ij}, y_{ij} from previously calculated or boundary values.

Calculation of the rate function, R, at each point involves solving the equations

$$R = \frac{dy}{dT} = \rho(x - x^*) = \sigma(y^* - y) \qquad (5\text{-}6)$$

$$\frac{y^*}{1 - y^*} = K \frac{x^*}{1 - x^*} \qquad (5\text{-}7)$$

Elimination of x* between equations gives the quadratic equation in y*

$$(y^*)^2 - \left[\frac{1 + \xi K}{\xi(K - 1)} + \frac{\alpha}{\xi}\right] y^* + \frac{\alpha K}{\xi(K - 1)} = 0$$

with $\alpha = x + \xi y$, noting that $\frac{\sigma}{\rho} = \xi = \frac{N_P}{N_F}$ independent of the basis chosen. The required root is that which lies in the range 0.0 to 1.0.

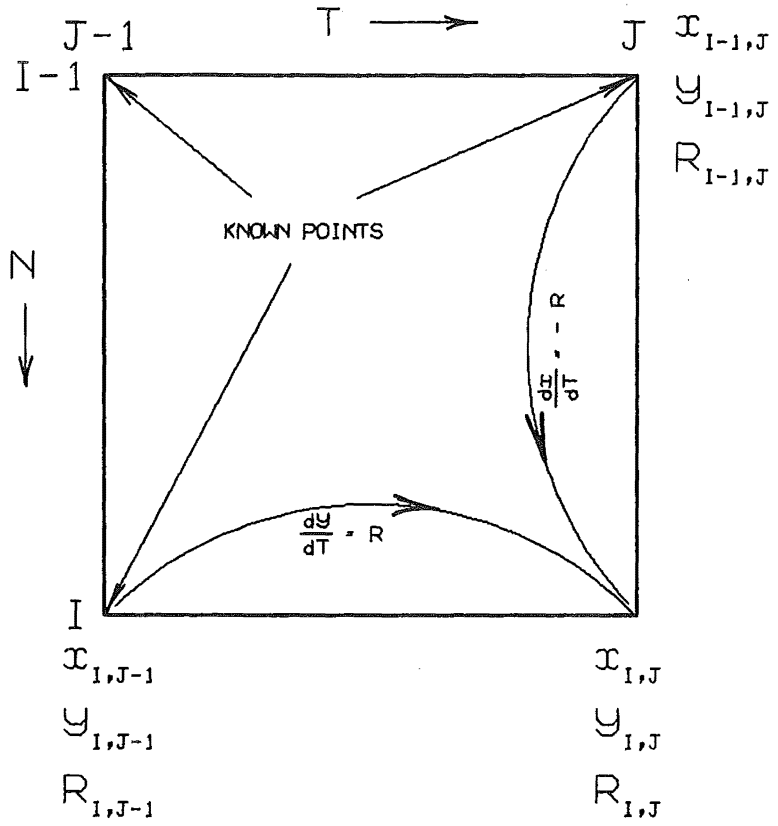


FIGURE 5-2. EQUATIONS AND VARIABLES AT EACH POINT IN THE FINITE-DIFFERENCE GRID.

CALCULATE FIRST ESTIMATES AT POINT $N = I * \Delta N$
$T = J * \Delta T$

$$x' = x_{I-1,J} - \Delta N * R_{I-1,J}$$
$$y' = y_{I,J-1} + \Delta T * R_{I,J-1}$$
$$R' = RATE(x', y')$$

CALCULATE SECOND ESTIMATES

$$x'' = x_{I-1,J} - \Delta N * R'$$
$$y'' = y_{I,J-1} + \Delta T * R'$$

CALCULATE FINAL VALUES AND RATE

$$x_{I,J} = \frac{(x' + x'')}{2}$$

$$y_{I,J} = \frac{(y' + y'')}{2}$$

$$R_{I,J} = RATE(x_{I,J}, y_{I,J})$$

FIGURE 5-3. CALCULATION AT EACH POINT IN THE FINITE-DIFFERENCE GRID.

Trial has shown that this is always that root with the discriminant taken with the negative sign.

The rate value, R, can be calculated from

$$R(x,y) = \sigma(y^* - y)$$

Some modification to this basic method is needed for:-

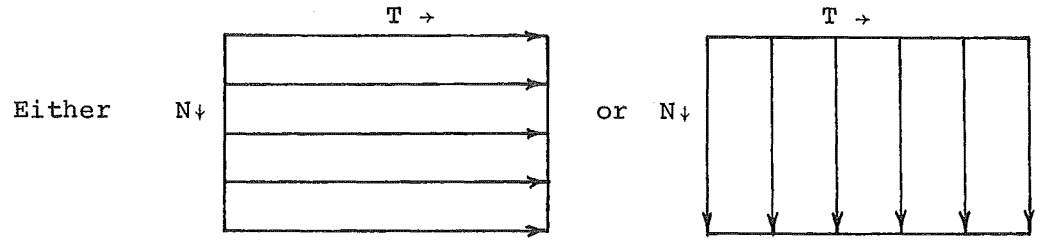
(a) Linear equilibrium, K = 1.

(b) Particle diffusion control, $\xi = 0.0$.

(c) Film diffusion control, $\xi = \infty$.

The modifications in each case are shown in Table 5-2, and Figure 5-4 shows a flow sheet for the rate calculation corresponding to the sub-program RATE in the IXLR program.

The point-to-point calculation can proceed along the constant T or the constant N characteristic.



The choice of primary calculation direction does not affect the method and has been decided by the function of the program. If break-through curves are required at a series of N', then the first is used, and IXLR is organised in this way. However, if the simulation is to be related to the passage of time for control purposes or if column operation is to depend on column behaviour (e.g. regeneration is to commence when the effluent concentration has risen to some limit) then the second method must be used.

Figure 5-5 is a flow-sheet of program IXLR using the point calculation method of Figure 5-3 and the rate calculation (Figure 5-4). The FORTRAN listing of IXLR is Appendix 5B with some sample results. An alternative program for the RATE function sub-program written in IBM 360 Assembler (IBM, 1966) is included in Appendix 5C and has in fact been used for all the results presented because of its superior speed to the FORTRAN version. Tests have shown that exactly the same results are obtained from each subprogram.

Conditions	Equations	Solution	Rate
Linear Equilibrium, K = 1	$(x - x^*) = \xi(y^* - y)$ $x^* = y^*$	$y^* = \frac{x + \xi y}{1 + \xi}$	$R = \sigma(y^* - y)$
Particle Control, $\xi = 0$	$x = x^*$	$y^* = \frac{K\,x}{1 + (K - 1)x}$	$R = y^* - y$
Film Control, $\xi = \infty$	$y^* = y$	$x^* = \frac{y}{y + K(1 - y)}$	$R = x - x^*$
General Conditions	$(x - x^*) = \xi(y^* - y)$ $\frac{y^*}{1 - y^*} = K\frac{x^*}{1 - x^*}$	$y^{*2} - \left[\frac{1 + \xi K}{\xi(K-1)} + \frac{\alpha}{\xi}\right]y^* + \frac{\alpha K}{\xi(K-1)} = 0$	$R = \sigma(y^* - y)$

TABLE 5-2 Equations used in IXLR, including modifications for limiting conditions.

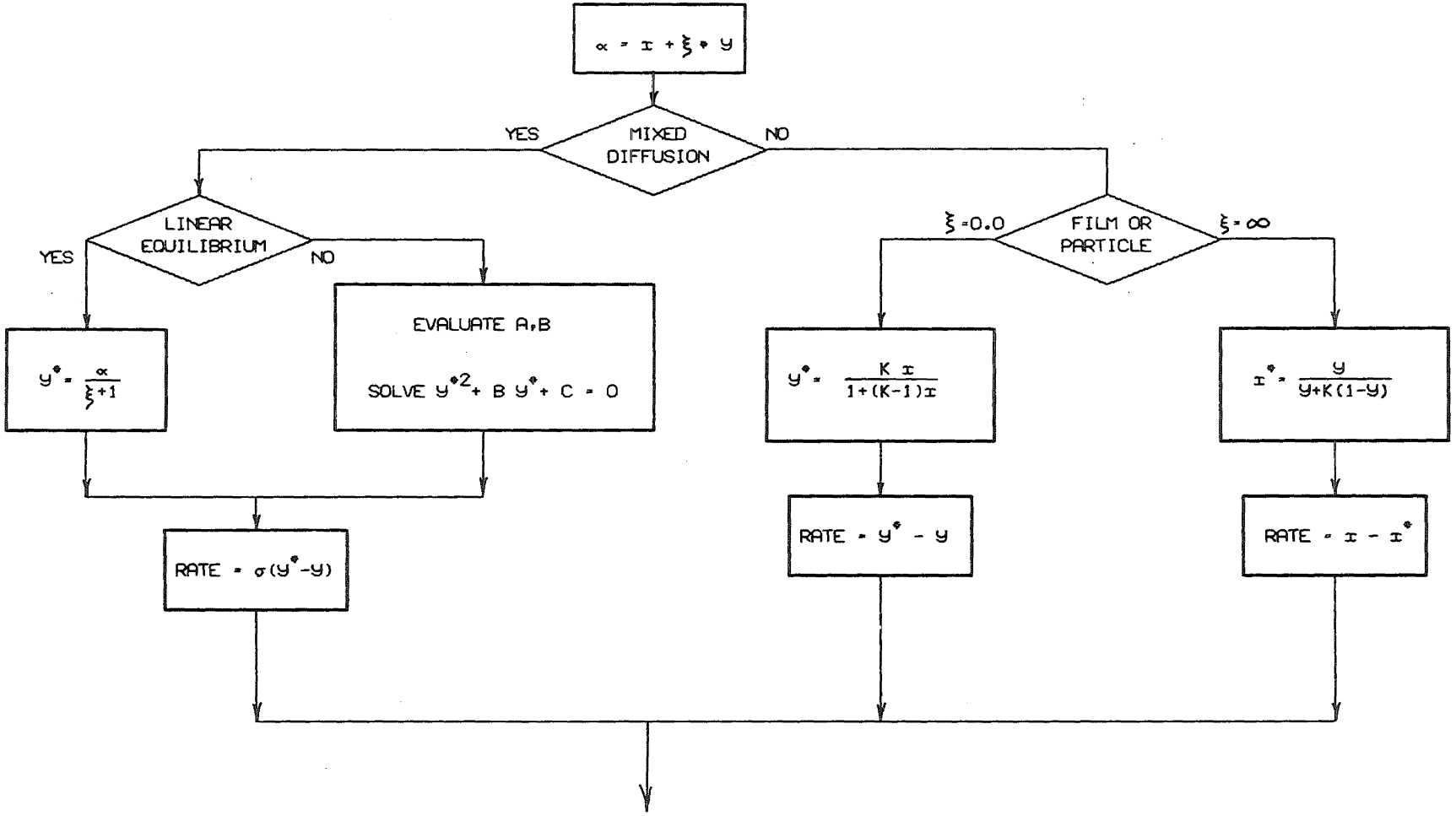


FIGURE 5-4. FLOW SHEET FOR RATE CALCULATION

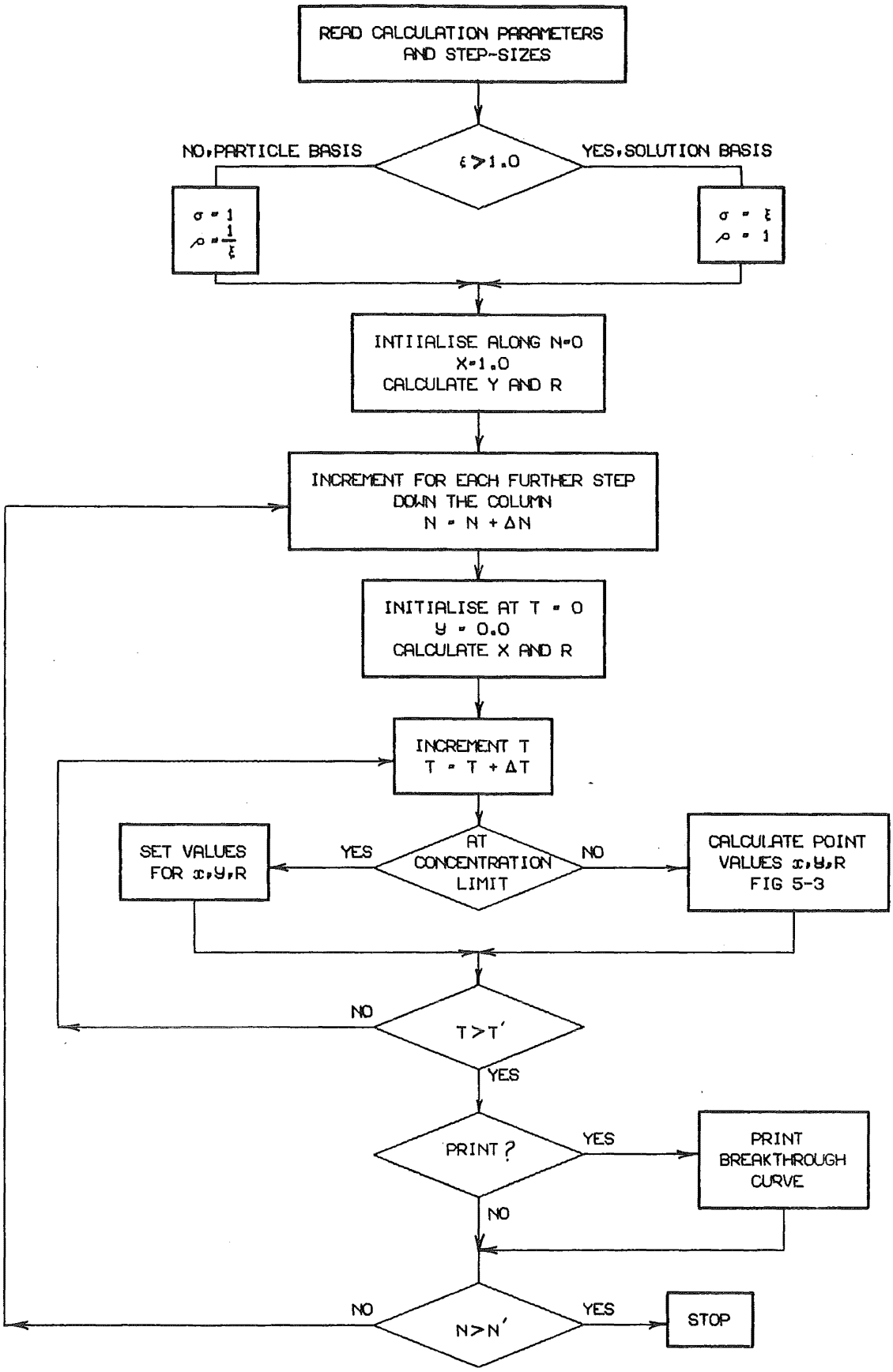


FIGURE 5-5. FLOW SHEET FOR IXLR.

Figure 5-6 is a typical response surface for the solution concentration on the N - T plane. Calculation in a proportion of the area is trivial because the column is either empty of solute or saturated. IXLR includes checks to minimise calculation in these regions.

5-4 Program Verification

Generally, the aim has been to attain accuracy of about ± 0.001 in computed solution and resin concentration ratios. Greater accuracy is possible, but irrelevant in terms of the accuracy of experimental data, fundamental properties and available correlations.

To prevent trivial computation, the column has been taken as saturated for x and y greater than 0.9999 or solute-free for x and y less than 0.0001.

Any computational scheme can produce incorrect results on five levels:-

(1) The equations of the model are wrong.

(2) The method of solution is wrong.

(3) The numerical method is wrong.

(4) The solution has not converged, i.e. the step size is too large or insufficient terms have been taken.

(5) There is a systematic error.

The purpose of this and the next section is to show how the last four possibilities have been minimised; the first must wait for the comparison against experimental data in Section 5-6.

IXLR can be tested against analytical results for linear equilibrium since, under this restriction, the equations solved are exactly those used by Thomas in deriving the J-function solution (Section 3-4).

Tables 5-3, 5-4, 5-5 list computed results for linear equilibrium for 10 and 50 transfer units for different values of the mechanism parameter. In each case, as the step-sizes ΔN and ΔT diminish, the IXLR values tend to the J function, in all cases within 0.0003. Presumably this divergence could be still further reduced with smaller step-sizes and tighter definition of saturation, provided that the rounding error does not become significant.

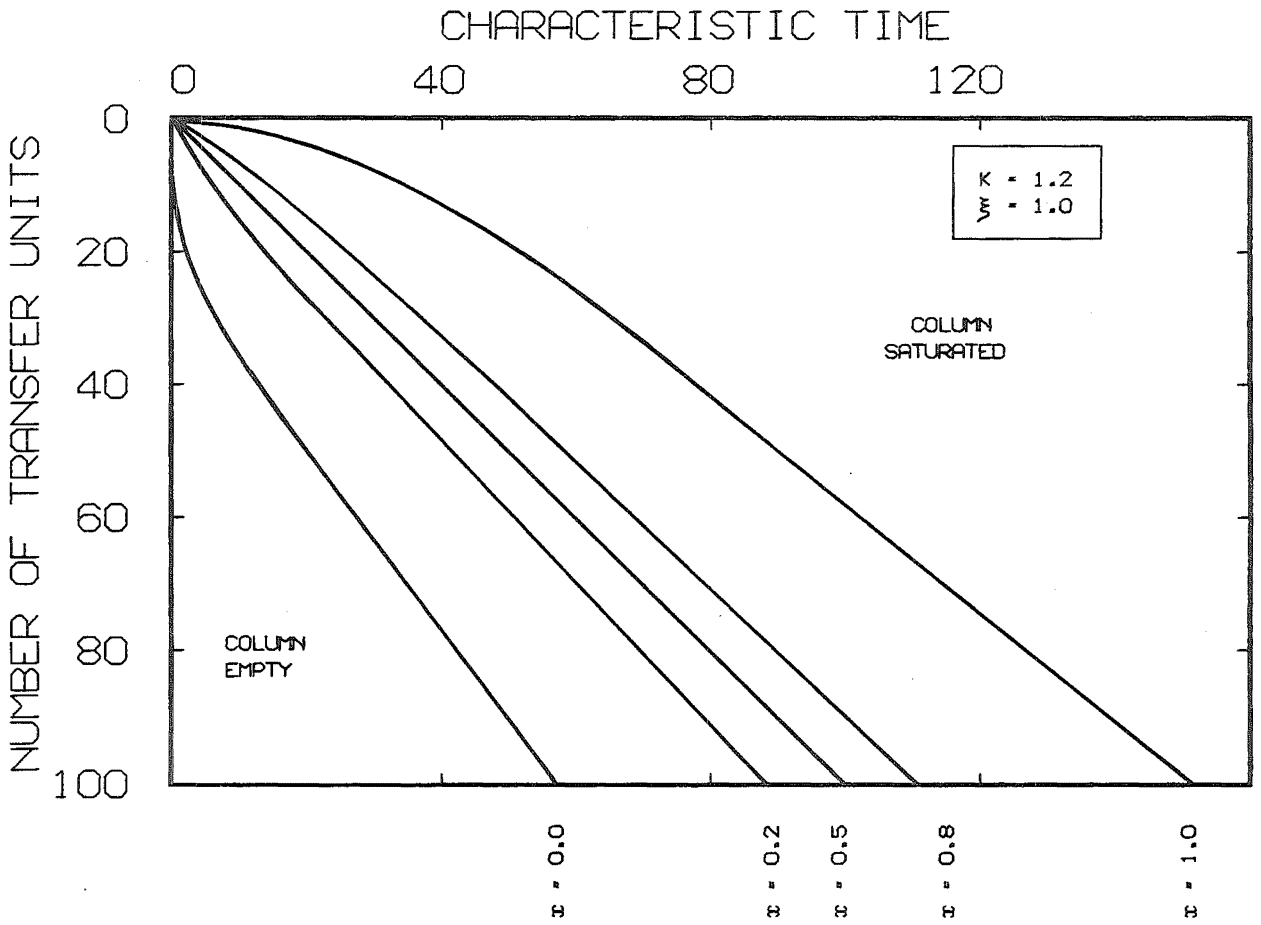


FIGURE 5-6. THE SOLUTION TO THE FIXED-BED EQUATIONS AS A CONTOUR SURFACE ABOVE THE N-T PLANE.

The J-function solution for linear equilibrium implies that computed breakthrough curves should be the same for the same values of N_R and T_R. For particle or film control ($\xi = 0$ or $\xi = \infty$), $N = N_R$, and the computed results for these two cases should be identical. This was found to be so for the IXLR results (at least for the four decimal places printed) and only one set of results is presented in Table 5-4. Similarly, Table 5-5 for $\xi = 0.1$ and 10.0 lists only one set of results, but in this case the IXLR results contained 5 values (marked with an asterisk) which differed by 0.0001 for the two ξ values.

The IXLR program has been verified for linear equilibrium. Three of the four paths through the RATE calculation (Figure 5-4) and all of the main program (Figure 5-5) have been covered. It remains therefore only to verify the fourth and most difficult path for non-linear equilibrium. A special program (Appendix 5C) was written to evaluate the RATE function at every combination of

x	y	ξ	k
0.0	0.0	0.0	0.1
0.5	0.5	0.1	0.5
1.0	1.0	0.5	1.0
		1.0	2.0
		2.0	10.0
		10.0	
		∞	

The rate function is independent of the number of transfer units, and this factor was not included.

Each of the 315 combinations has been checked to ensure that Eqns 5-6, 5-7 are satisfied by the calculated values for R, x* and y*. (cf. Appendix 5C). No inconsistency has been found.

The IXLR program can therefore be accepted as providing a correct solution to the equations of the model. However, further checks of its correctness can be made as results are produced:-

(a) The effluent concentration should tend smoothly to the feed concentration as the column becomes saturated.

(b) The overall mass balance can be checked, provided the break-

N = 10		IXLR				J Function
	ΔN	1.0	0.5	0.25	0.125	
	T					
	2	.0561	.0629	.0651	.0655	.0656
	4	.1551	.1675	.1685	.1686	.1686
	6	.2884	.2990	.2986	.2983	.2982
	8	.4324	.4369	.4356	.4352	.4351
	10	.5675	.5658	.5644	.5640	.5639
	12	.6824	.6770	.6758	.6756	.6756
	14	.7736	.7671	.7664	.7663	.7663
	16	.8425	.8367	.8364	.8364	.8365
	20	.9279	.9252	.9255	.9255	.9256
	22	.9523	.9509	.9513	.9513	.9514
	26	.9799	.9799	.9802	.9803	.9804
	30	.9920	.9923	.9925	.9925	.9926
	Area	10.015	10.000	9.9993	9.9997	
	Maximum convergence error	0.0135	0.0027	0.0005	0.0001	
N = 50	T					
	26	.0270	.0289	.0293	.0294	.0295
	30	.0618	.0645	.0649	.0650	.0651
	36	.1571	.1599	.1601	.1601	.1601
	40	.2494	.2512	.2510	.2509	.2510
	46	.4157	.4151	.4146	.4144	.4144
	50	.5309	.5291	.5285	.5283	.5283
	56	.6878	.6854	.6849	.6847	.6848
	60	.7735	.7714	.7712	.7711	.7712
	66	.8694	.8684	.8684	.8683	.8685
	70	.9133	.9130	.9131	.9131	.9132
	80	.9729	.9733	.9735	.9735	.9736
	90	.9929	.9933	.9934	.9933	.9934
	Area	50.017	50.000	49.999	49.999	
	Maximum convergence error	0.0034	0.0009	0.0002	0.0002	
	Computation time (secs)	8	20	44	123	

TABLE 5-3. Comparison of IXLR results with those from the J function.

K = 1.0 ξ = 1.0

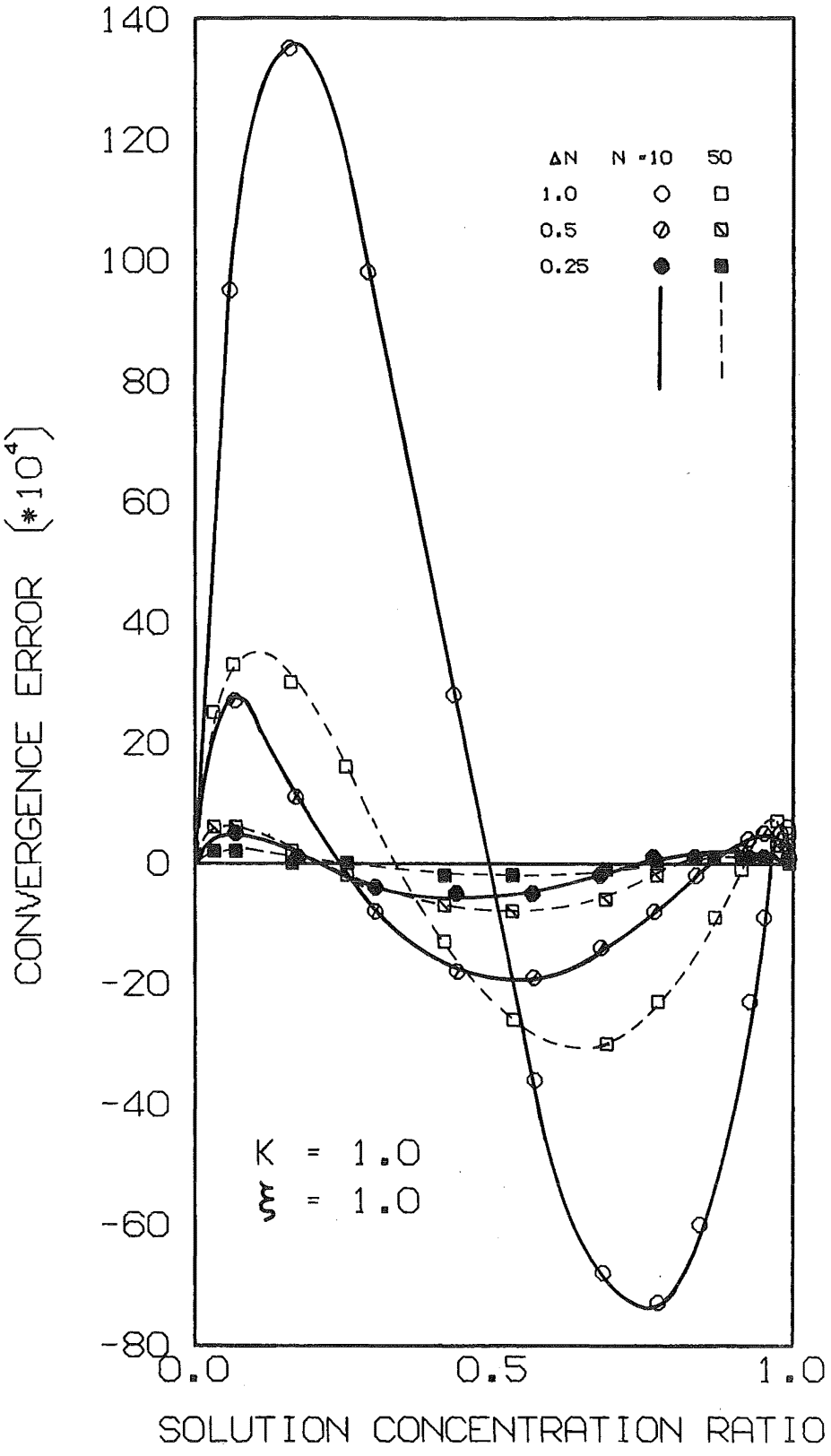
		IXLR			J Function
N = 10	ΔN 1.0	0.5	0.25	0.125	
	T				
	2 Unstable	.0086	.0097	.0103	.0105
	4	.0599	.0652	.0662	.0665
	6	.1825	.1892	.1895	.1894
	8	.3604	.3631	.3624	.3621
	10	.5485	.5462	.5452	.5449
	12	.7086	.7044	.7037	.7035
	14	.8257	.8221	.8219	.8219
	16	.9021	.9003	.9004	.9005
	18	.9479	.9475	.9478	.9479
	20	.9735	.9738	.9741	.9742
	22	.9871	.9876	.9878	.9879
	24	.9940	.9944	.9945	.9945
	Area	10.010	10.000	9.9996	
	Maximum convergence error	0.0074	0.0013	0.0004	
N = 50	T				
	25 Unstable	.0017	.0018	-	.0021
	30	.0129	.0136	.0138	.0140
	35	.0552	.0568	-	.0572
	40	.1564	.1578	-	.1580
	45	.3224	.3225	.3222	.3221
	50	.5219	.5205	-	.5200
	55	.7062	.7047	-	.7044
	60	.8426	.8419	.8418	.8419
	65	.9260	.9261	-	.9263
	70	.9692	.9696	-	.9698
	75	.9886	.9890	.9890	.9891
	80	.9963	.9965	-	.9965
	Area	50.007	49.998	49.999	
	Maximum convergence error	0.0022	0.0005	0.0002	
	Computation time (secs)	16	33	81	

TABLE 5-4. Comparison of IXLR results with those from the J function.
K = 1.0 $\xi = 0$ and ∞

		IXLR			
N = 11	ΔN	1.0	0.5	0.25	0.125	$\bar{J}$ Function
(N_R = 10)	T					
	2.2	unstable	.0086	.0097	.0103	.0105
	4.4		.0599	.0652*	.0662	.0665
	6.6		.1825	.1892	.1895	.1894
	8.8		.3604	.3631	.3624	.3621
	11.0		.5485	.5462	.5452	.5449
	13.2		.7086	.7043*	.7037	.7035
	15.4		.8257	.8221*	.8219	.8219
	17.6		.9021	.9003	.9004	.9005
	19.8		.9479	.9475	.9478*	.9479
	22.0		.9735	.9738	.9741	.9742
	24.2		.9871	.9876	.9878	.9879
	26.4		.9940	.9944	.9945	.9945
	Area		11.011	11.000	11.000	
	Maximum convergence error		0.0074	0.0013	0.0004	
N = 55	T					
(N_R = 50)	29.7	unstable	.0041	.0045	.0046	.0048
	36.3		.0326	.0339	.0342	.0344
	42.9		.1306	.1322	.1324	.1325
	49.5		.3224*	.3225	.3222	.3221
	56.1		.5614	.5599	.5594	.5594
	62.7		.7674	.7661	.7659	.7659
	69.3		.8984	.8982	.8982	.8984
	75.9		.9630	.9633	.9634	.9636
	82.5		.9886	.9890	.9890	.9891
	89.1		.9971	.9973	.9973	.9972
	Area		55.008	54.999	54.999	
	Maximum convergence error		0.0022	0.0005	0.0002	
	Computation time (secs)		15	35	94	

*indicates results which differ by 0.0001 for the two mechanism parameter values used.

TABLE 5-5 Comparison of IXLR results with those from the J function. K = 1.0 ξ = 0.1 and 10.0



GRAPH 5-1. THE EFFECT OF STEP-SIZE ON THE CONVERGENCE OF IXLR.

through curve is continued until the column is saturated, in the form (Eqn 2-28)

$$\int_{x=o}^{x=1} (1 - x)\, dT = N'$$

where N' should agree with the number of transfer units for which the breakthrough curve is being computed.

The integral is equally spaced and can be evaluated using Simpson's rule.

(c) As each breakthrough curve is printed, it should include those variables necessary (x, y, R, x*, y*) to check Eqns 5-6 and 5-7.

5-5 Step-Size Selection

The step-size in T has been maintained at twice that in N,

i.e. $\Delta T = 2\Delta N$.

This was justified in that the range of T required is about twice that in N, and the same number of steps would then be taken in each direction. A small number of trials supported this decision.

The required step-size for a desired level of accuracy can be determined for linear equilibrium from Tables 5-3, 5-4 and 5-5. The convergence error has been defined as the difference between the J function and the IXLR computed value. The maximum convergence error was determined for each step-size from a graph such as Graph 5-1 and has been included in the tables as a measure of the worst error arising from a large step-size. Also included are the computing time and the area above the breakthrough curve.

The computing time was the time taken to compute to N' = 50 and T' = 100. The time for spooled input-output operations is included in the computing time, and is the time to read one punched card and to print 5 breakthrough curves, each about 25 lines.

Graph 5-1 shows that the area test is not useful for indicating step-size convergence since the convergence error is distributed fairly evenly about zero. Some fluctuation in the third decimal place of the computed area, particularly for small step-sizes, is due to the

quadrature method.

The conclusions to be drawn from the step-size tests at linear equilibrium are:-

(a) that at a step-size of $\Delta N = 0.25$ the largest maximum convergence error is 0.0013 at $N = 10$ and $\xi = 0$. This is acceptable in terms of the accuracy required.

(b) that the maximum convergence error is smaller at 50 transfer units, and larger step-sizes could be used for larger columns.

(c) that the step-size could be made slightly larger at $\xi = 1$ than at $\xi = 0$ or infinity.

Similar results have been compiled in Tables 5-6, 5-7 for favourable ($K = 5.0$) and unfavourable ($K = 0.2$) equilibrium. For non-linear equilibrium the convergence error cannot be defined in terms of a known solution, nor strictly in terms of the results at $\Delta N = 0.125$ since these may not quite be at convergence. Since for Heun's method (Eqn 5-5) the error for one step is proportional to $(\Delta N)^3$ and the number of steps is inversely proportional to ΔN, the total error will be proportional to $(\Delta N)^2$. Halving the step-size should reduce the convergence error to one-quarter, in reasonable agreement with Graph 5-1. The convergence error has been taken as 1.25 times the error between results at any step-size and at $\Delta N = 0.125$.

At favourable equilibrium, smaller step-sizes are required, but at $\Delta N = 0.25$ the maximum convergence error is still only 0.002, and the average error less. The convergence error is not reduced at 50 transfer units, presumably because constant pattern conditions have been attained.

Unfavourable equilibrium allows a slightly larger step-size.

From these trials, all results have been computed with $\Delta N = 0.25$, $\Delta T = 0.5$, except at very favourable equilibrium ($K > 5$) when these step-sizes have been halved.

	ΔN	1.0	0.5	0.25	0.125
N = 10	T				
	2	.0040	.0029	.0027	.0027
	4	.0172	.0134	.0129	.0128
	6	.0640	.0527	.0517	.0514
	8	.2193	.1850	.1838	.1833
	10	.5995	.5066	.5035	.5022
	12	.9822	.8238	.8186	.8184
	14	1.0000	.9450	.9470	.9480
	16	1.0000	.9827	.9854	.9861
	18	1.0000	.9946	.9961	.9964
	20	1.0000	.9985	.9990	.9991
	Area	9.2555	9.9895	9.9983	9.9992
	Maximum Convergence error	0.170	0.0083	0.0019	
N = 50	T				
	44	.0960	.0150	.0144	.0142
	46	.3233	.0544	.0532	.0529
	48	.7780	.1861	.1844	.1838
	49	-	.3220	.3202	.3191
	50	1.0000	.5054	.5017	.5002
	51	1.0000	.6892	.6824	.6810
	52	1.0000	.8217	.8163	.8160
	54	1.0000	.9439	.9459	.9468
	56	1.0000	.9822	.9850	.9856
	58	1.0000	.9944	.9959	.9962
	Area	46.47	49.986	49.998	50.000
	Maximum Convergence error	0.78	0.0022	0.0022	
	Computation time (secs)	2	9	26	98

TABLE 5-6 Effect of step-size on IXLR results.

K = 5.0 ξ = 1.0

	ΔN	1.0	0.5	0.25	0.125
	T				
N = 10	1	-	.2550	.2571	.2569
	2	.3530	.3611	.3602	.3597
	4	.5049	.5057	.5038	.5033
	6	.6037	.5996	.5983	.5980
	8	.6711	.6660	.6651	.6650
	10	.7200	.7155	.7150	.7149
	15	-	.7980	.7979	.7978
	20	.8496	.8491	.8491	.8491
	40	.9431	.9432	.9433	.9433
	60	.9776	.9776	.9776	.9776
	80	.9919	.9919	.9919	.9918
	Area	-	-	-	-
	Maximum convergence error	.0085	.0042	.0009	
	T				
N = 50	2	.0084	.0076	.0087	.0091
	5	-	.0557	.0576	.0580
	10	.1817	.1893	.1895	.1895
	15	-	.3138	.3134	.3133
	20	.4112	.4116	.4111	.4110
	30	.5482	.5468	.5465	.5464
	40	.6357	.6346	.6344	.6343
	50	.6972	.6965	.6964	.6963
	60	.7433	.7428	.7428	.7427
	80	.8085	.8084	.8084	.8083
	100	.8531	.8531	-	-
	Area	-	-	-	-
	Maximum convergence error	.0117	.0036	.0006	
	Computation time (secs)	13	36	88	294

TABLE 5-7 Effect of step-size on IXLR results

K = 0.2 ξ = 1.0

5-6 Comparison with Experimental Results

The verification of the program IXLR has shown that it correctly solves the equations of the model. However, the model itself may be faulty in that its equations may be wrong or its assumptions untenable. The purpose of this section is to compare computed breakthrough curves with experimental results and so justify both the model of the fixed-bed ion exchange process, as well as its method of solution.

The experimental data used were obtained by Kelly (1966) and the range covered is shown in Table 5-8. There are thirteen breakthrough curves, both for complete exhaustion and complete regeneration. Most contain results from more than one run. The separation factors shown were independently measured by Kelly, and the numbers of transfer units are taken from Kelly's Table IV, having been calculated from standard correlations and fundamental properties (Hiester et al., 1956).

5-6-1 Complete Exhaustion

Graphs 5-2 to 5-14 show the experimental and computed exhaustion breakthrough curves. With two exceptions, the agreement is good. If the number of transfer units for these two curves is modified, without changing the separation factor or the mechanism parameter, then these also come into good agreement. The two are:-

System	Runs	Graph	Transfer Units Calculated	Best Fit
0.1 N Na-H	69, 70, 71	5-5	46	75
0.1 N Na-Li	93, 94	5-13	102	75

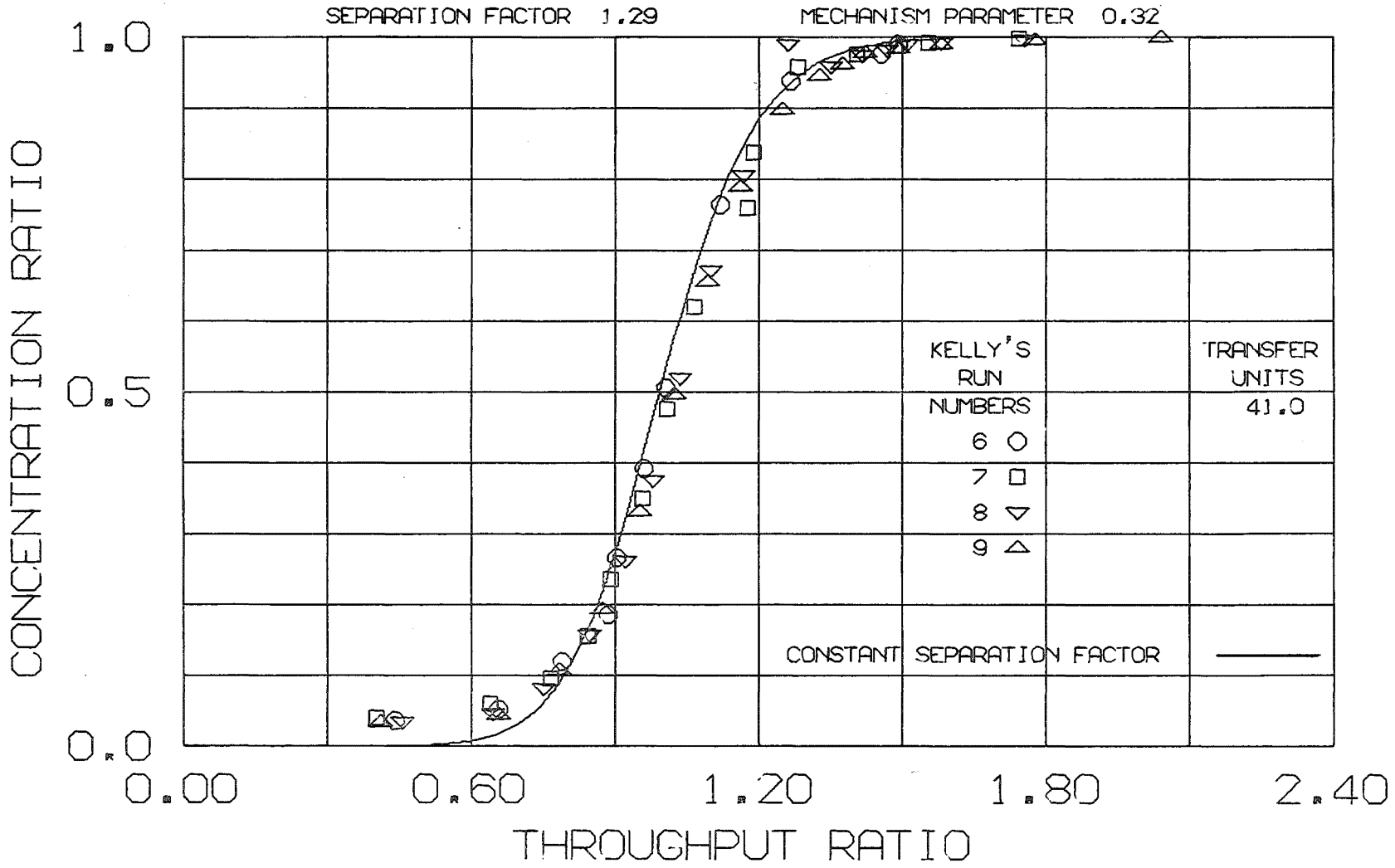
By using the mid-point slopes of the breakthrough curves for the experimental data, Kelly (his Table V) calculates the equivalent number of reaction transfer units to be:-

System	N_R	b	N (from Eqn 3-24)
0.1 N Na-H	66	1.19	77
0.1 N Na-Li	61	1.32	70

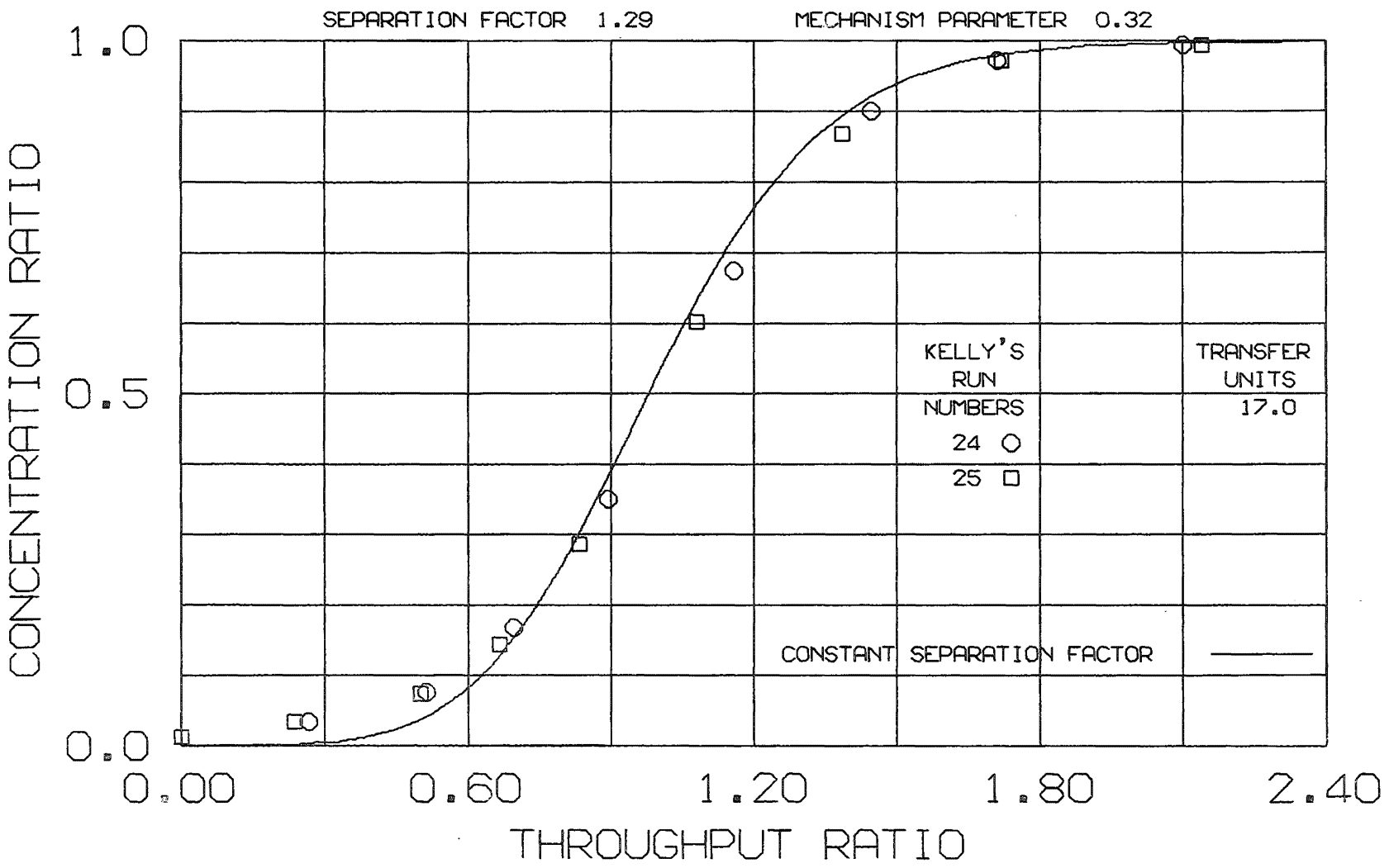
These values are in better agreement with the best fit from IXLR. There is apparently some conflict between the predicted column parameters and the breakthrough behaviour for these two systems. The equivalent regeneration curves (Graphs 5-18 and 5-26) are in agreement with the above best-fit values, suggesting that the correlation is at fault. Moison (1959) has suggested that there is a bed-depth effect for short beds,

Run Numbers	System	Normality	Bed Factor	Flow Factor	N_p	N_f	ξ	K Exhaustion	K re-generation	Graphs Exhaustion	Graphs Regeneration
6-9	Na/H	1.0	1.0	1.0	41	133	0.32	1.29	0.77	5-2	5-15
24-25	Na/H	1.0	0.4	1.0	17	63	0.32	1.29	0.77	5-3	5-16
37-39	Na/H	0.1	1.0	1.0	376	146	2.6	1.48	0.68	5-4	5-17
69-71	Na/H	0.1	1/3	1.0	118	46	2.6	1.48	0.68	5-5	5-18
74-76	Na/H	0.1	2/3	1.0	247	96	2.6	1.48	0.68	5-6	5-19
79-81	Na/H	0.1	4/3	1.0	505	197	2.6	1.48	0.68	5-7	5-20
84-85	Na/H	0.1	1.0	1/2	746	207	3.65	1.48	0.68	5-8	5-21
86	Na/H	0.1	1.0	1/4	1508	294	5.1	1.48	0.68	5-9	5-22
87-88	H/Li	0.1	1.0	1.0	284	121	2.4	1.29	0.77	5-10	5-23
89-90	H/K	0.1	1.0	1.0	529	176	3.0	2.20	0.45	5-11	5-24
91-92	Na/K	0.1	1.0	1.0	265	115	2.3	1.56	0.64	5-12	5-25
93-94	Na/Li	0.1	1.0	1.0	189	102	1.9	1.92	0.52	5-13	5-26
95-96	Na/Ca	0.1	1.0	1.0	51	95	0.54	8.6	0.12	5-14	5-27

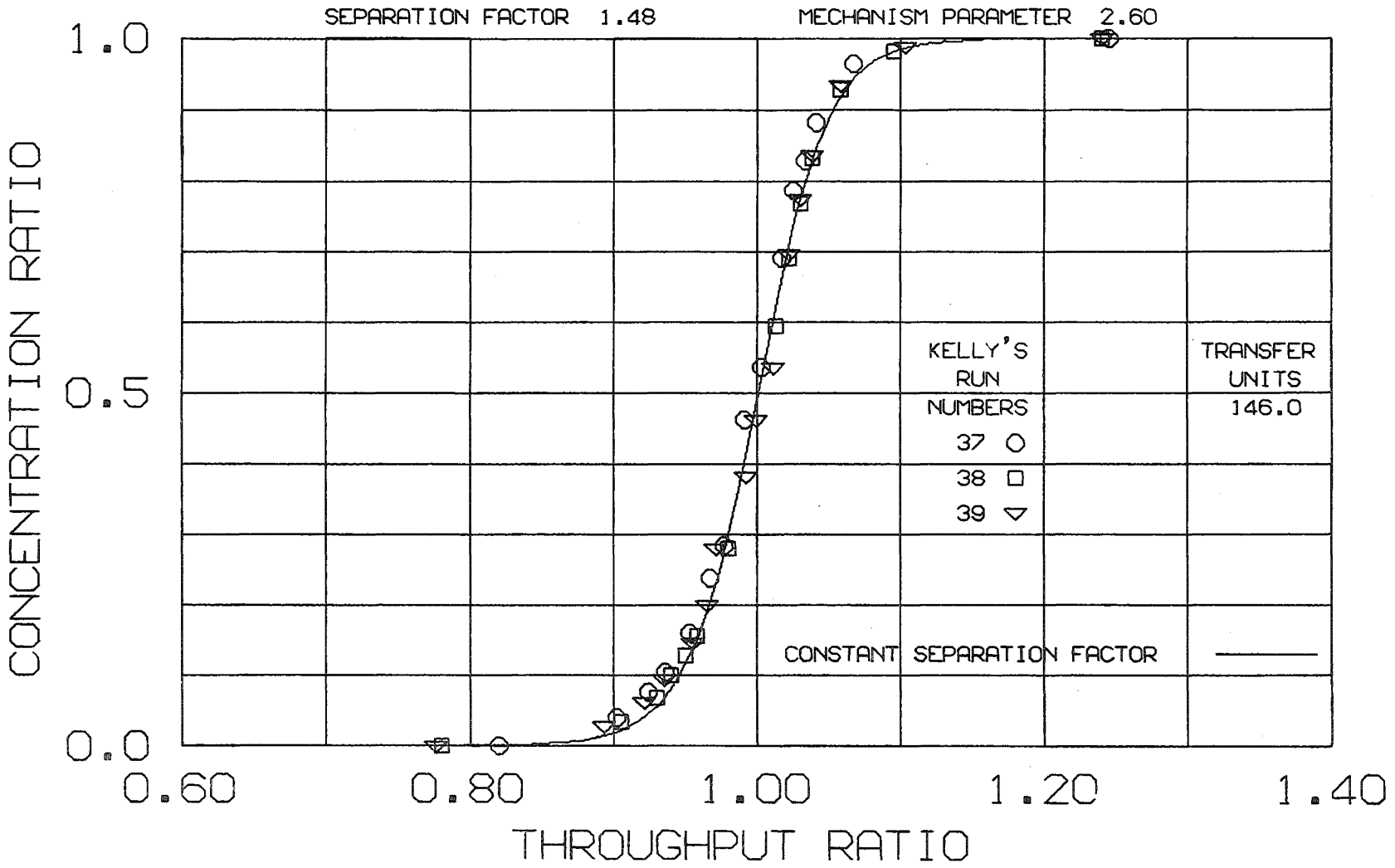
TABLE 5-8. Summary of parameters for experimental breakthrough curves.



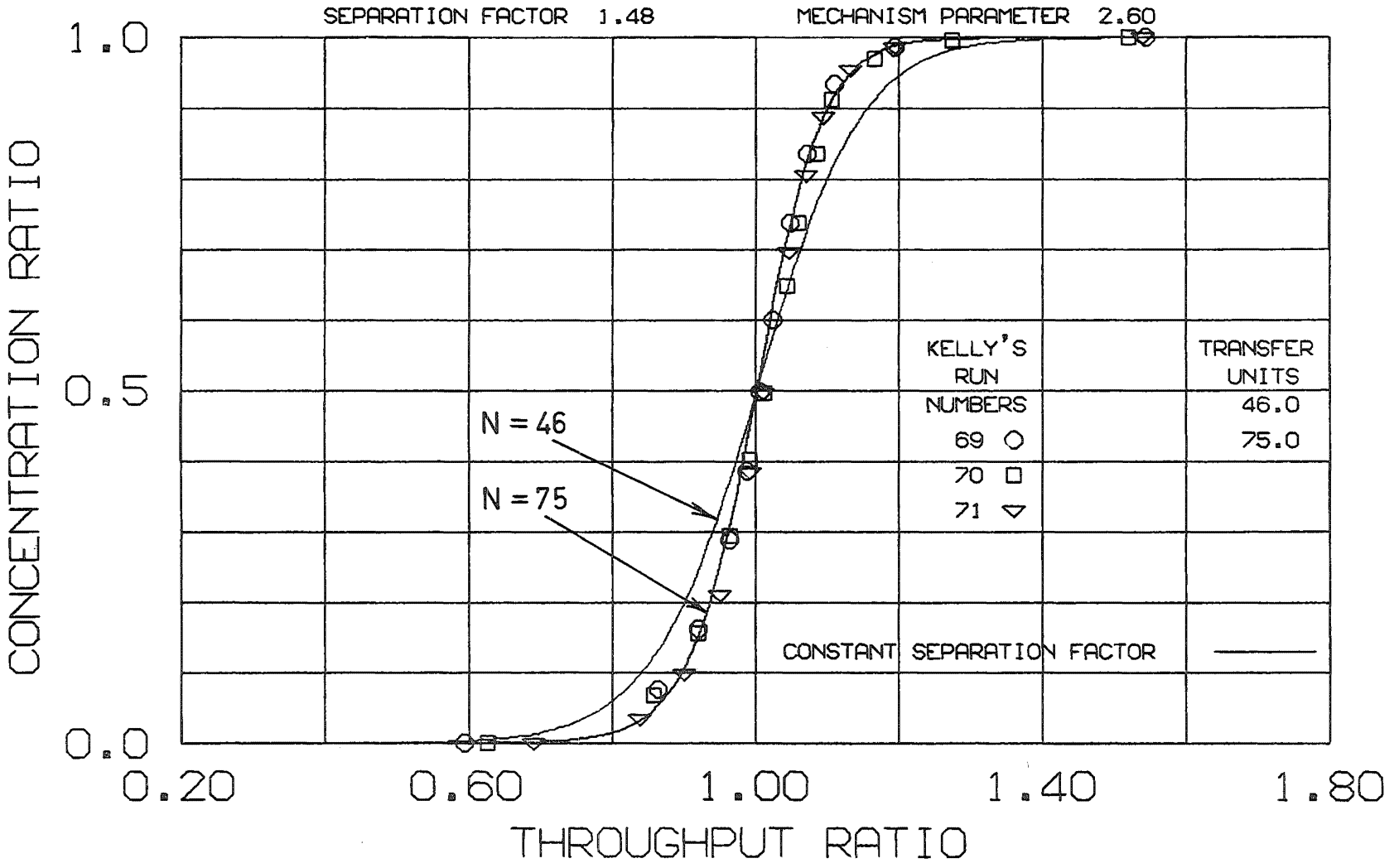
GRAPH 5-2. COMPUTED AND EXPERIMENTAL BREAKTHROUGH CURVES, 1. ON NA--H-CL EXHAUSTION.



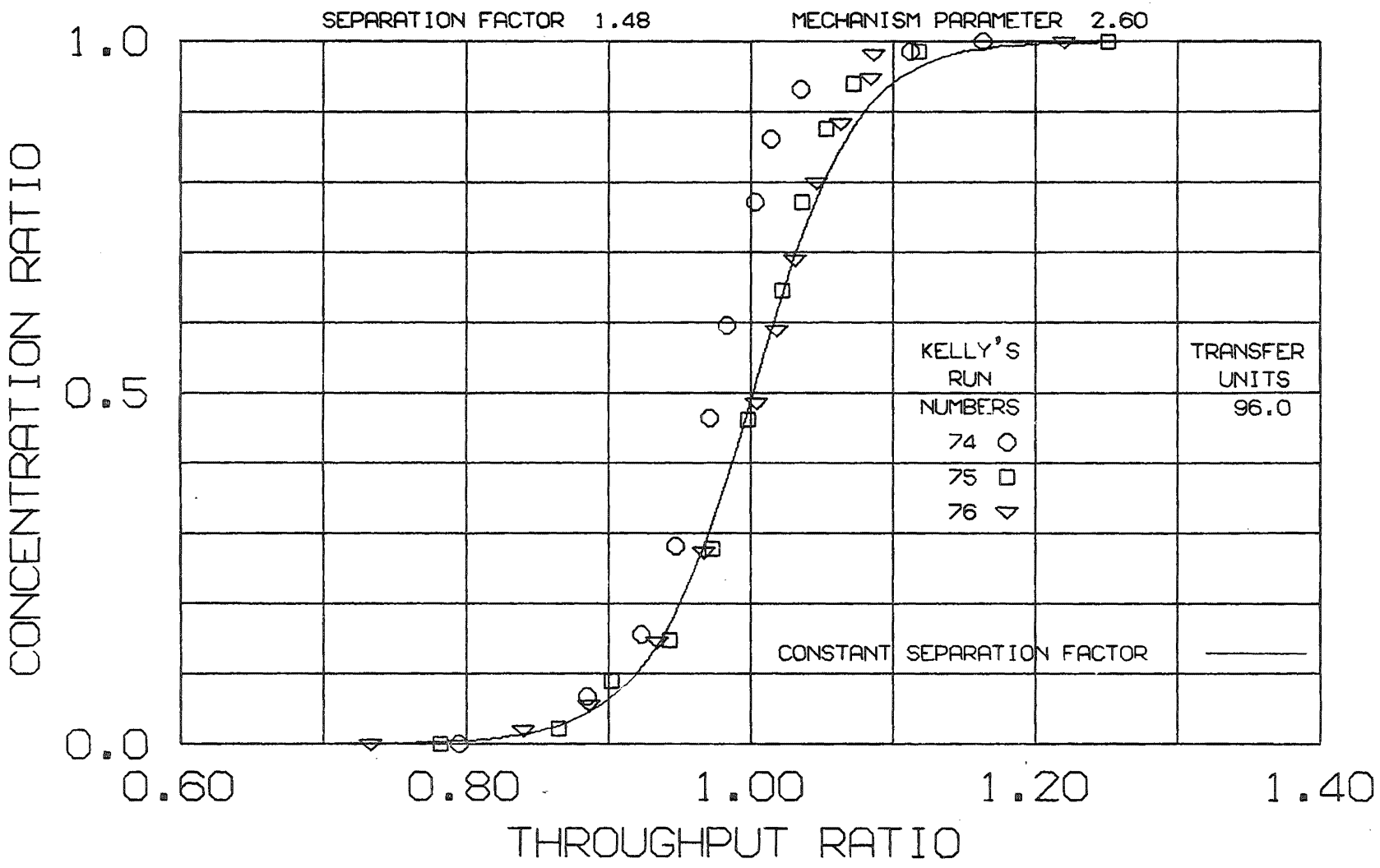
GRAPH 5-3. COMPUTED AND EXPERIMENTAL BREAKTHROUGH CURVES, 1. ON NA-H-CL EXHAUSTION.



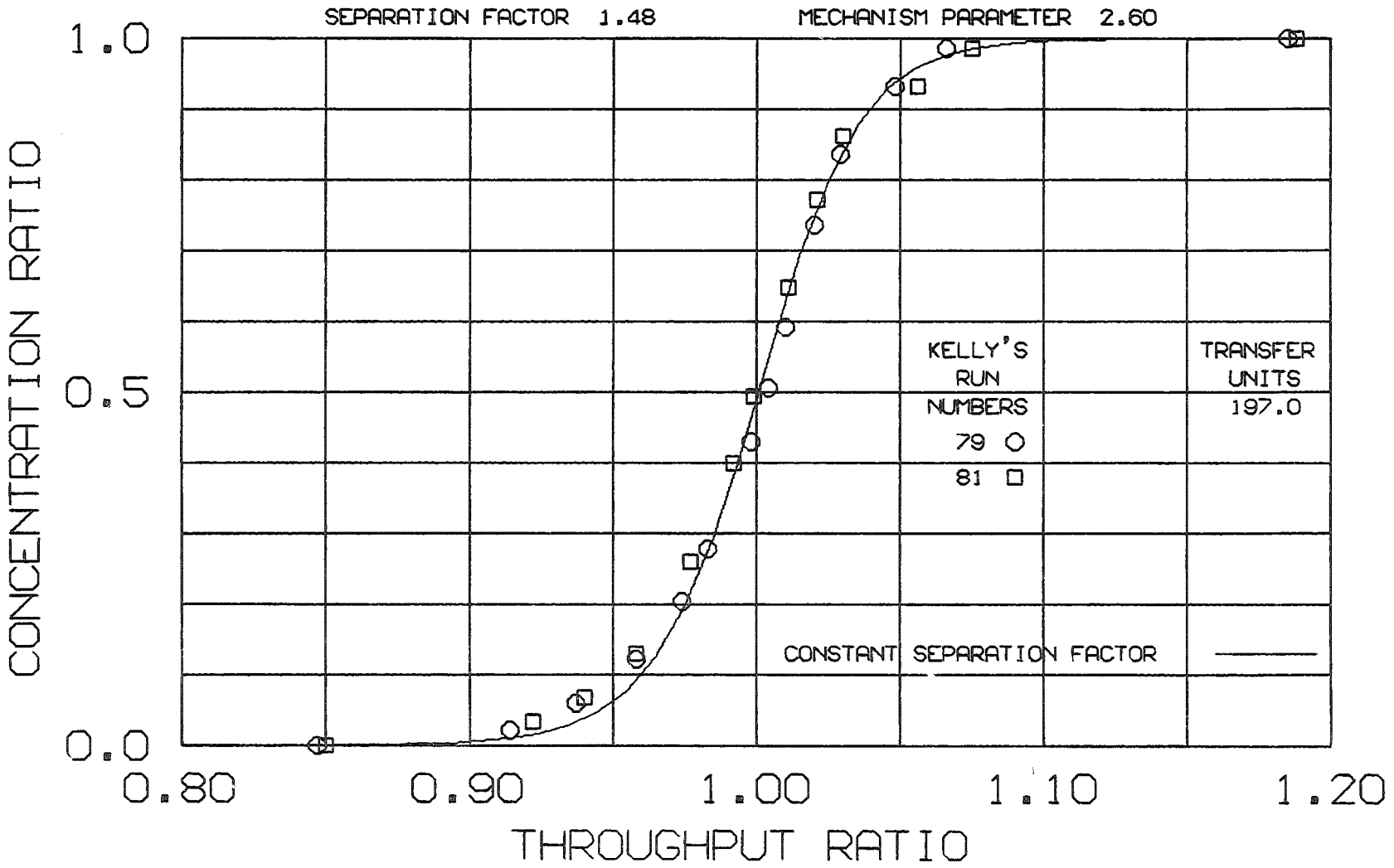
GRAPH 5-4. COMPUTED AND EXPERIMENTAL BREAKTHROUGH CURVES, 0.1N NA-H-CL EXHAUSTION.



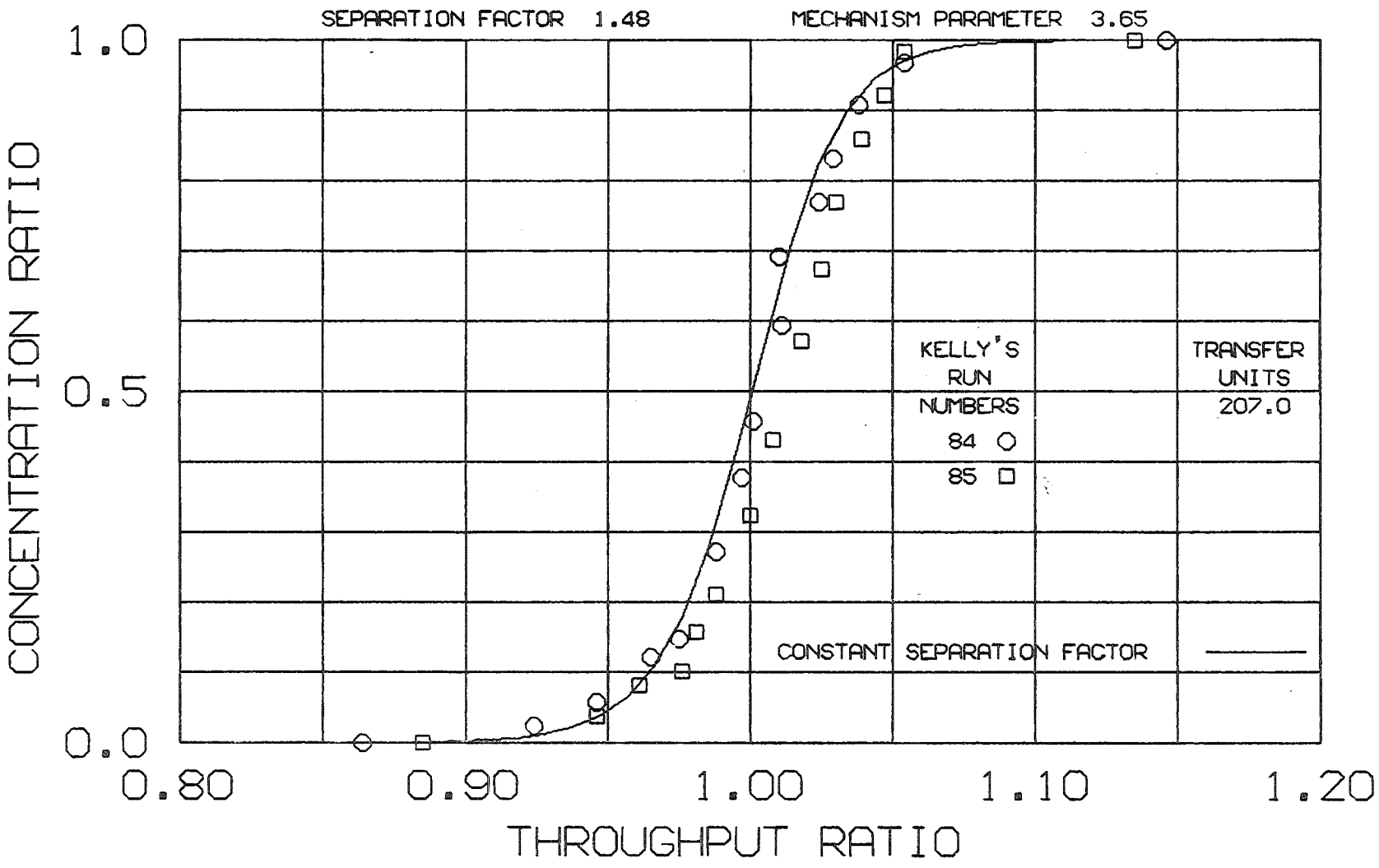
GRAPH 5-5. COMPUTED AND EXPERIMENTAL BREAKTHROUGH CURVES, 0.1N NA-H-CL EXHAUSTION.



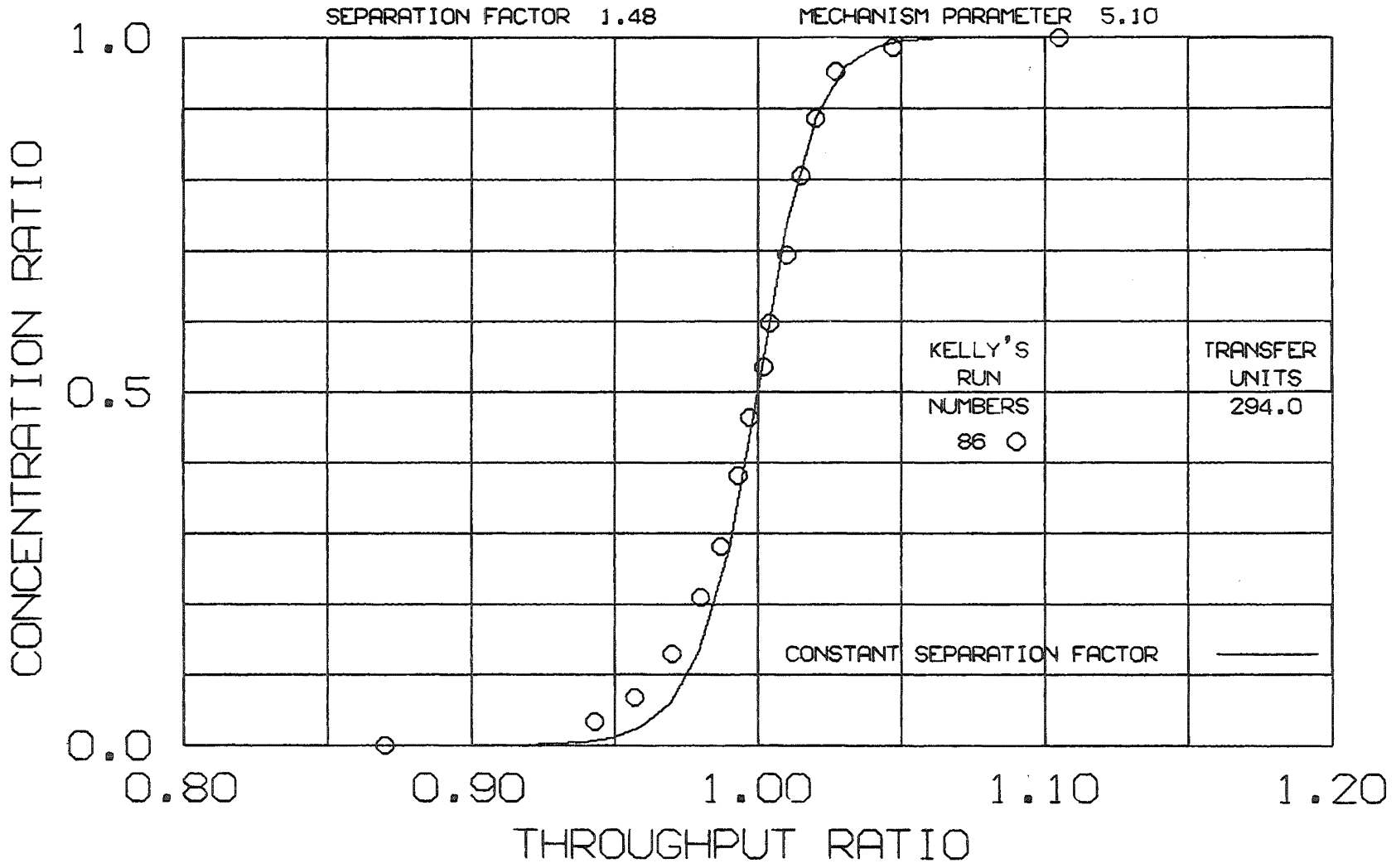
GRAPH 5-6. COMPUTED AND EXPERIMENTAL BREAKTHROUGH CURVES, 0.1N NA-H-CL EXHAUSTION.



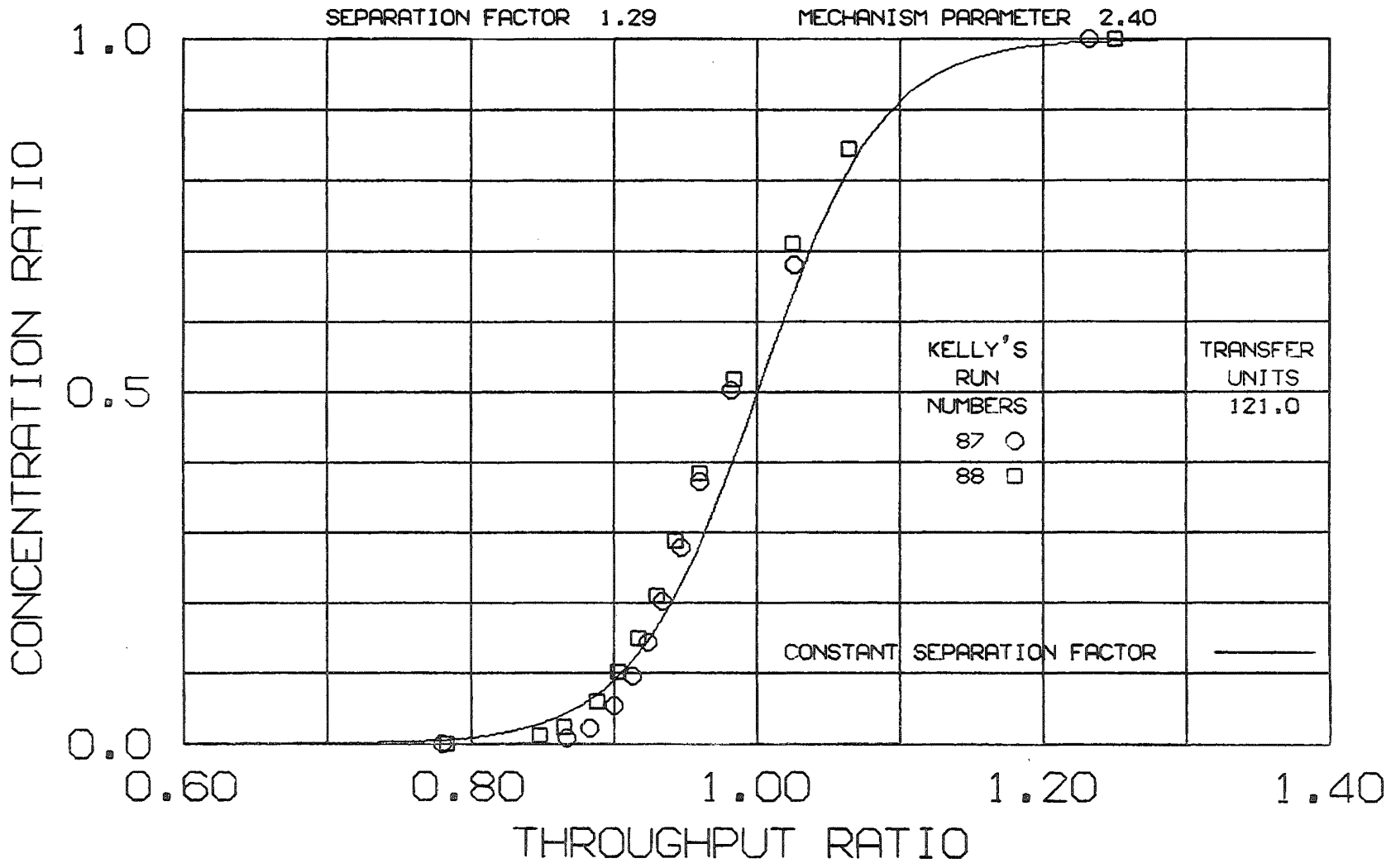
GRAPH 5-7. COMPUTED AND EXPERIMENTAL BREAKTHROUGH CURVES, 0.1N NA-H-CL EXHAUSTION.



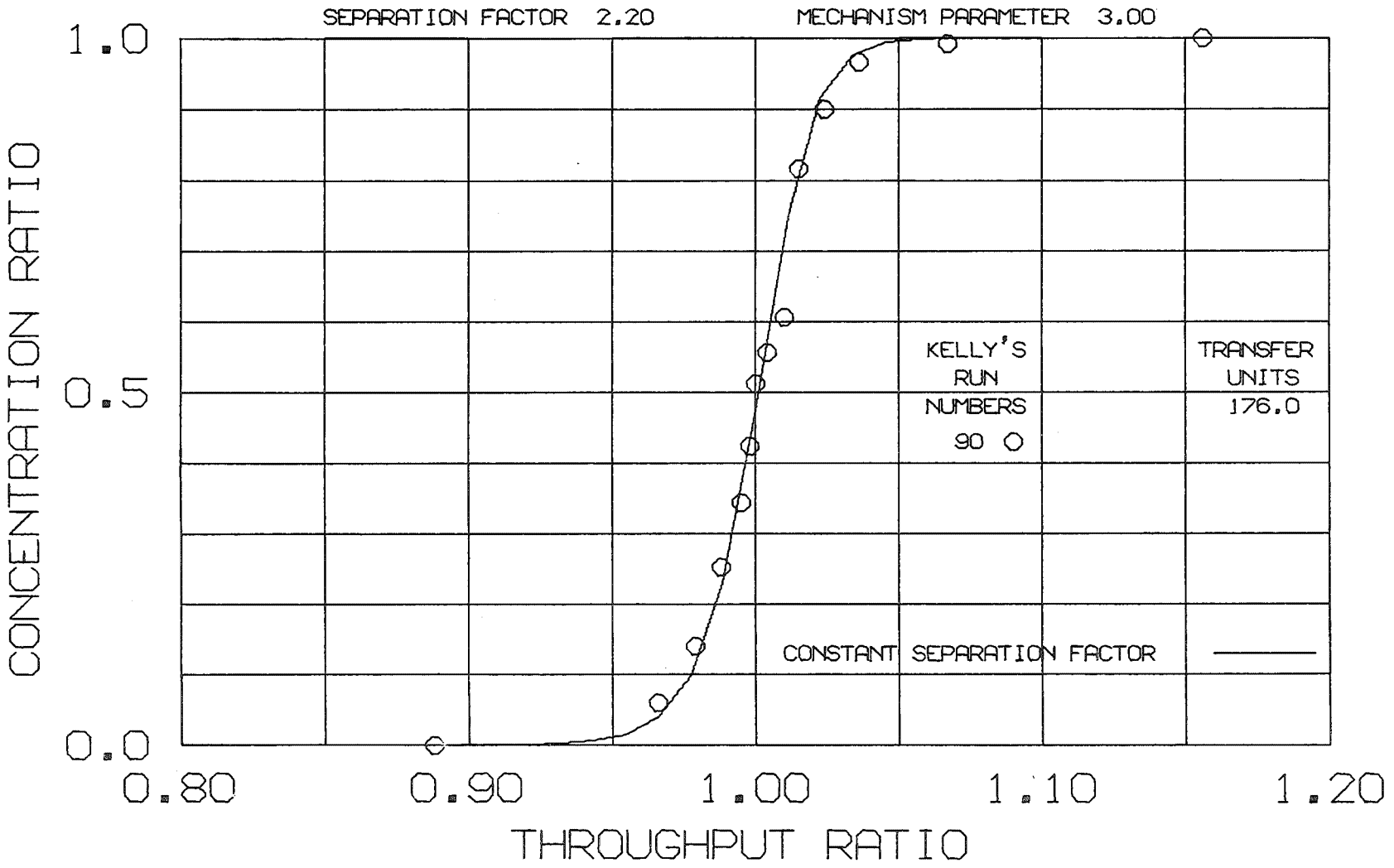
GRAPH 5-8. COMPUTED AND EXPERIMENTAL BREAKTHROUGH CURVES, 0.1N NA-H-CL EXHAUSTION.



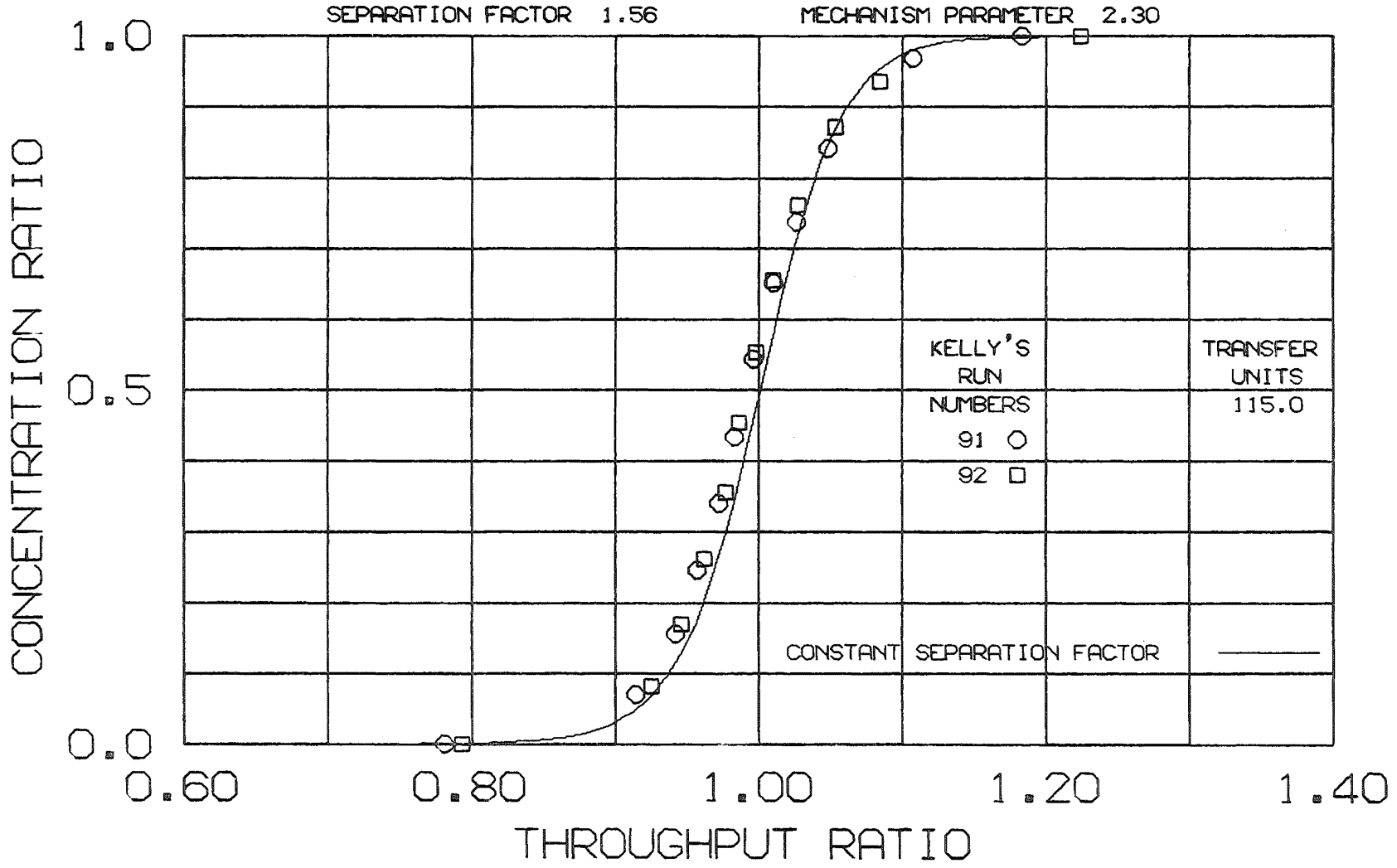
GRAPH 5-9. COMPUTED AND EXPERIMENTAL BREAKTHROUGH CURVES, 0.1N NA-H-CL EXHAUSTION.



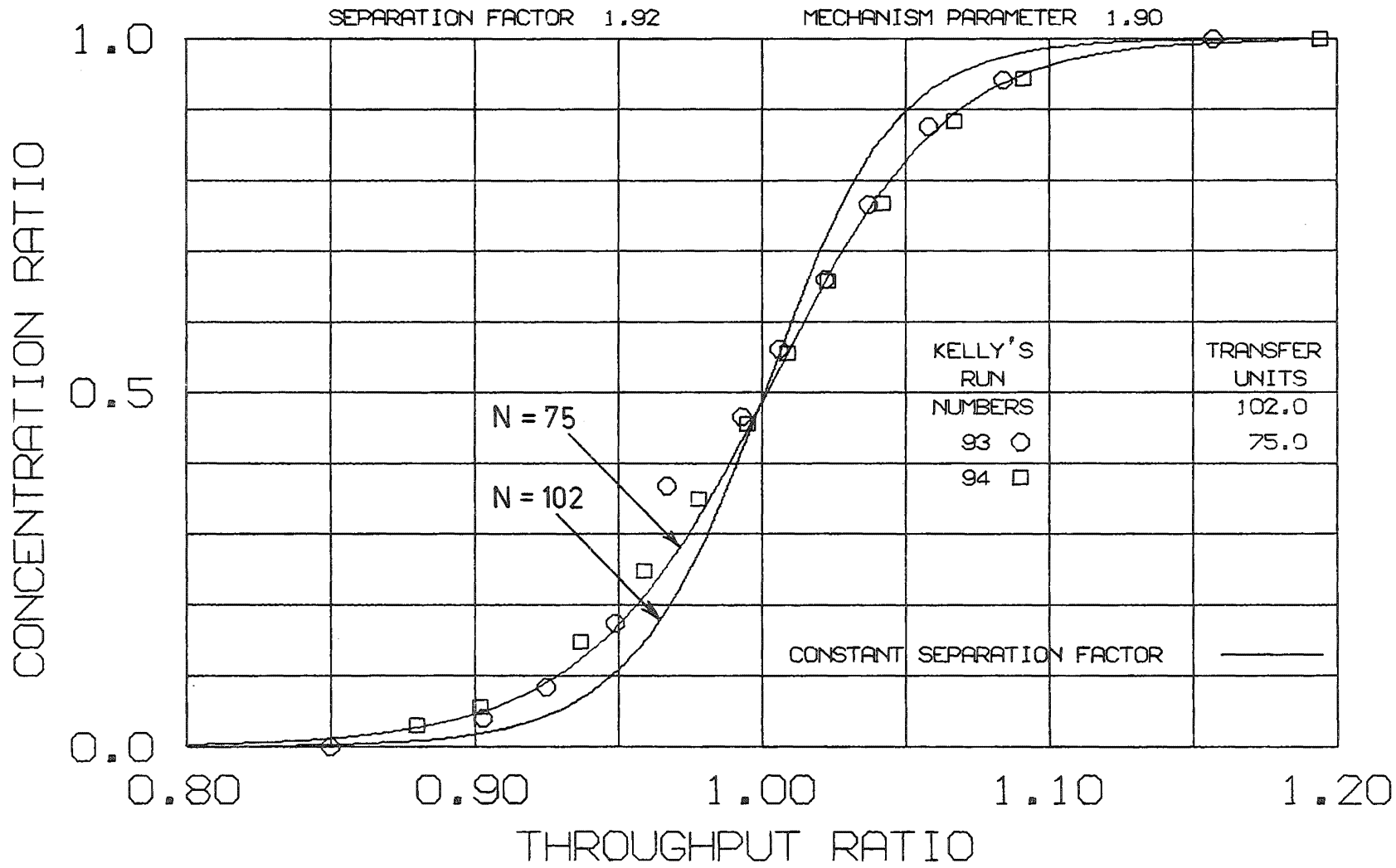
GRAPH 5-10. COMPUTED AND EXPERIMENTAL BREAKTHROUGH CURVES, 0.1N H-LI-CL EXHAUSTION



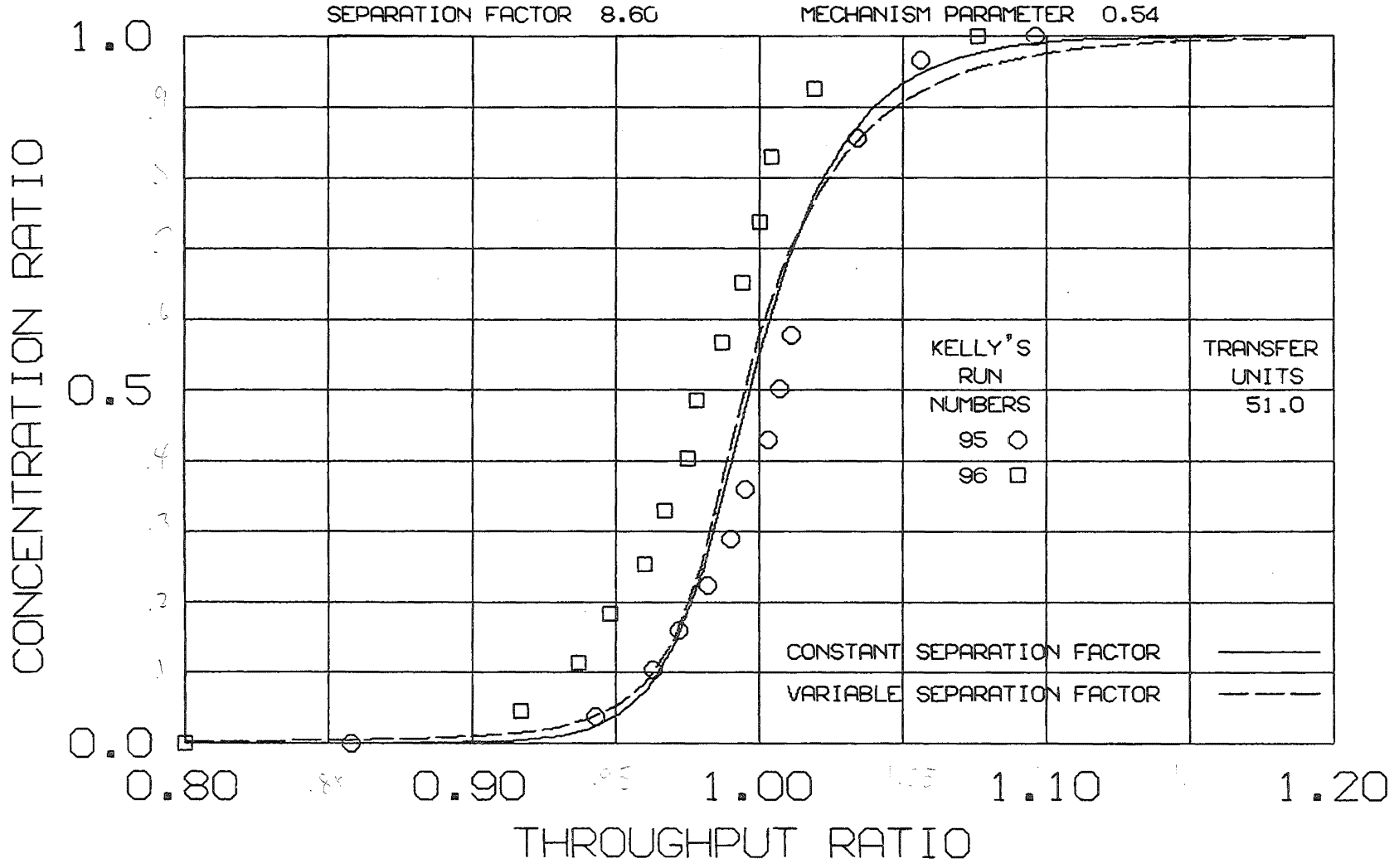
GRAPH 5-11. COMPUTED AND EXPERIMENTAL BREAKTHROUGH CURVES, 0.1N K-H-CL EXHAUSTION.



GRAPH 5-12. COMPUTED AND EXPERIMENTAL BREAKTHROUGH CURVES, 0.1N K-NA-CL EXHAUSTION.



GRAPH 5-13. COMPUTED AND EXPERIMENTAL BREAKTHROUGH CURVES, 0.1N NA-LI-CL EXHAUSTION.



GRAPH 5-14. COMPUTED AND EXPERIMENTAL BREAKTHROUGH CURVES, 0.1N CA-NA-H EXHAUSTION.

which may explain Graph 5-5.

Graph 5-14 is the breakthrough curve for the calcium-sodium system, and is of interest because the exchanging ions are not of the same valency and the separation factor will be only approximately constant. While there is a clear difference in the replications (accentuated by the expanded throughput ratio scale) and while the computed breakthrough curve passes generally over the data points of Run 96, the shape of the computed curve is not quite that of the data. This can be attributed to the variation in selectivity.

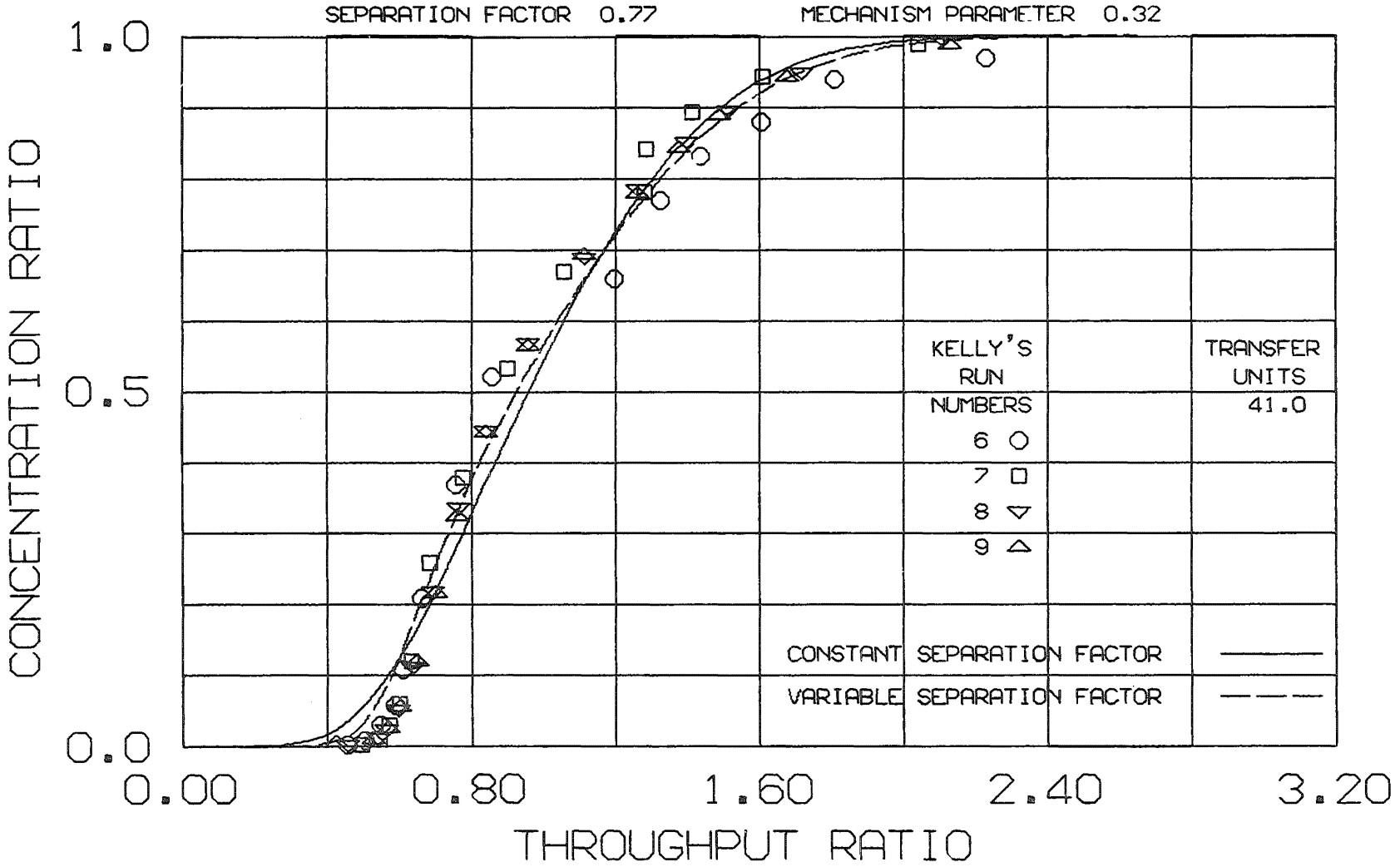
The data points for 1.0 normal breakthrough curves (Graphs 5-2 and 5-3) before breakthrough are not zero. Kelly (1966) has explained this effect in terms of differential resin swelling and electrolyte accumulation as the resin changes from one ionic form to another in concentrated solution.

5-6-2 Complete Regeneration

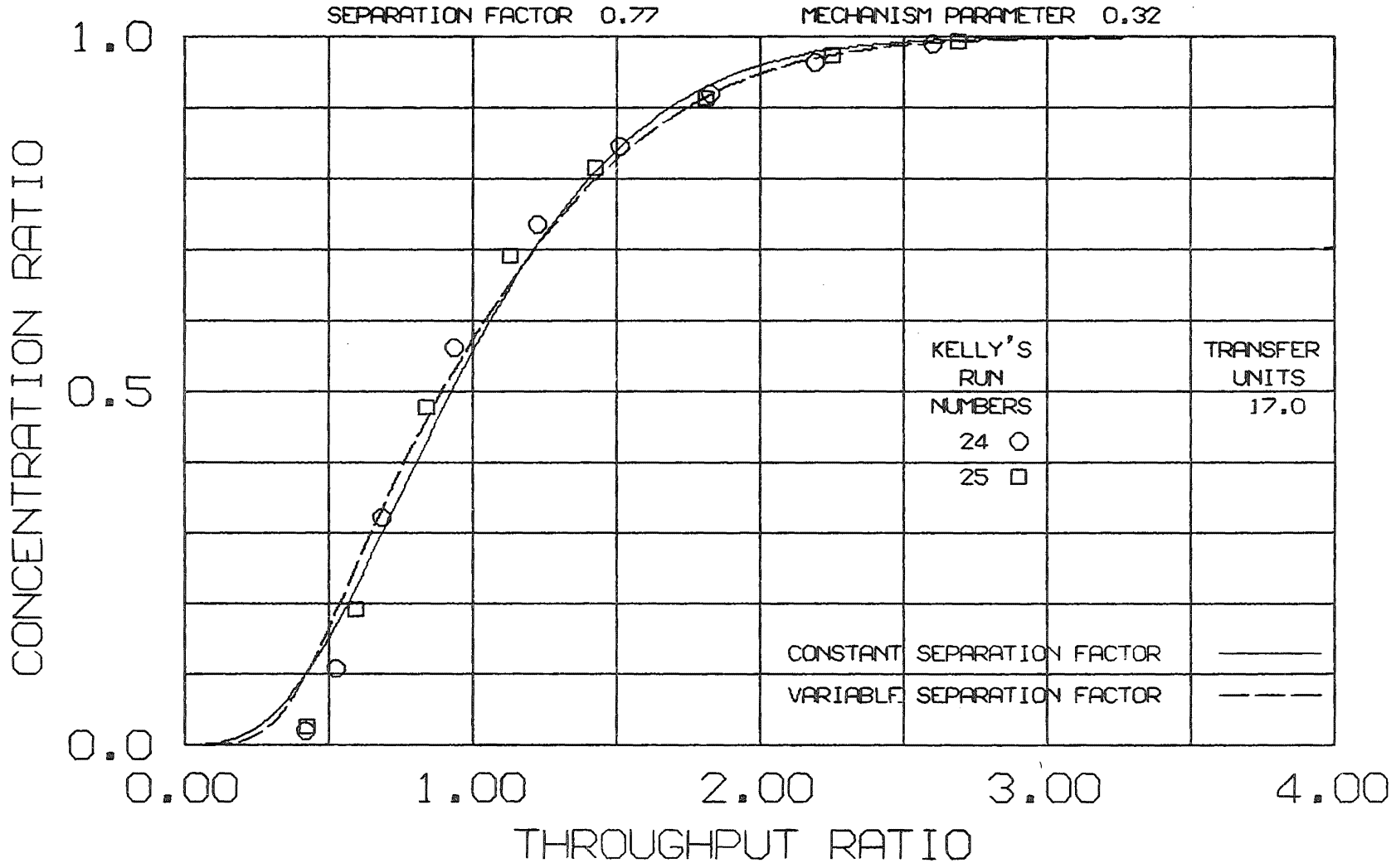
The equivalent plots for complete regeneration are Graphs 5-15 to 5-27. The agreement between computed and experimental breakthrough curves is good only for the H-Li, K-Na and Na-Li systems (Graphs 5-23, 5-25 and 5-26). The other graphs (with the exception of the Ca-Na system, Graph 5-27, which will be separately treated later) have a characteristically different shape to that of the data in that the predicted solution concentration rises too soon and too gradually.

Kelly's equilibrium results provide the reason. Graph 5-28 shows the variation in the separation factor with solution concentration. Three systems (H-Li, K-Na and Na-Li) have a reasonably constant separation factor. For the other systems (1.0N and 0.1N Na-H, Ca-Na, K-H) the separation factor varies strongly, and these are exactly those systems for which the computed curves do not match the data.

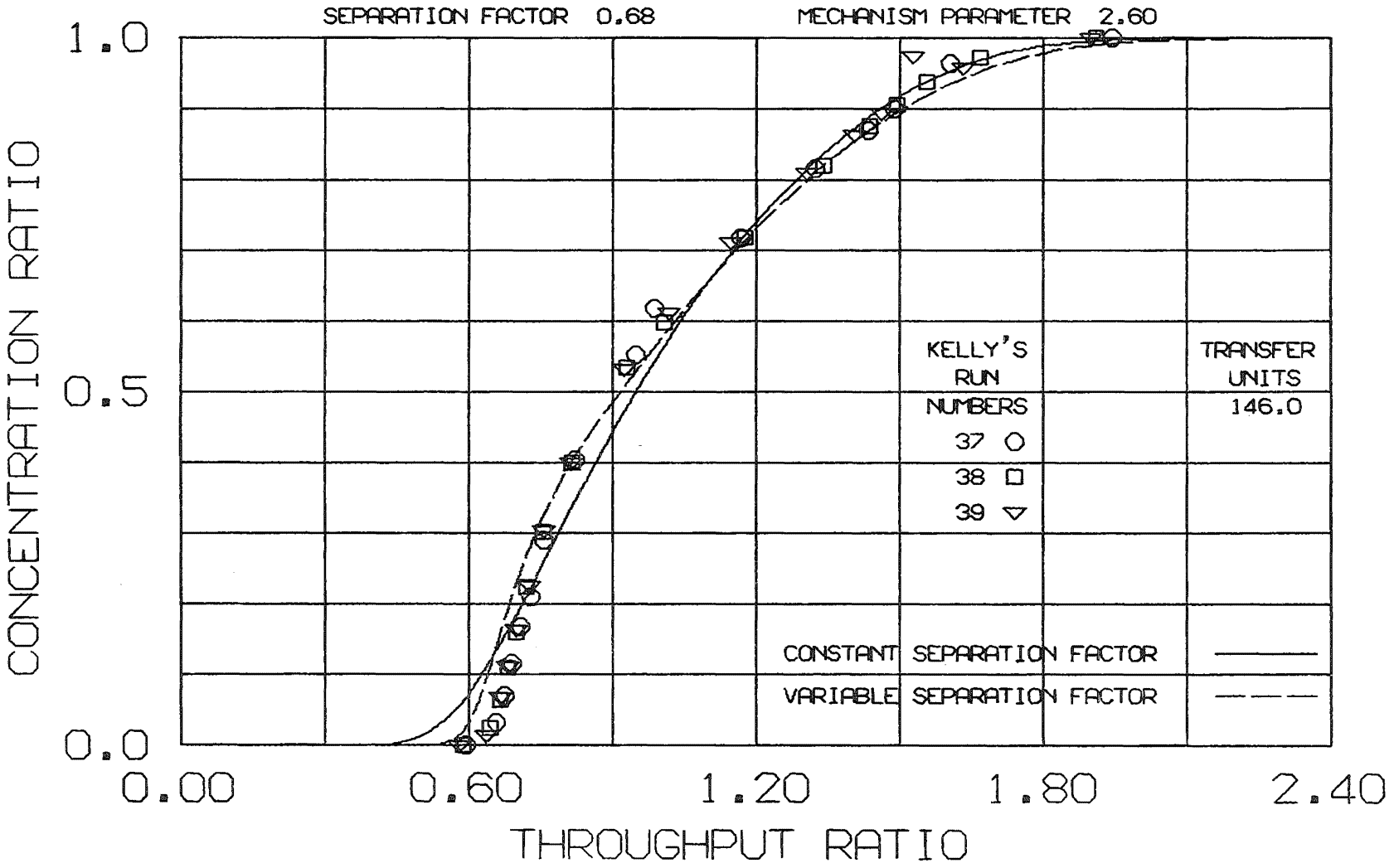
The next section discusses a modification to IXLR to allow the separation factor to be a function of the interfacial solution concentration. As the graphs show, following this modification, the computed breakthrough curves match the experimental data. Graph 5-24 is perhaps the clearest demonstration of the need for a concentration-dependent separation factor.



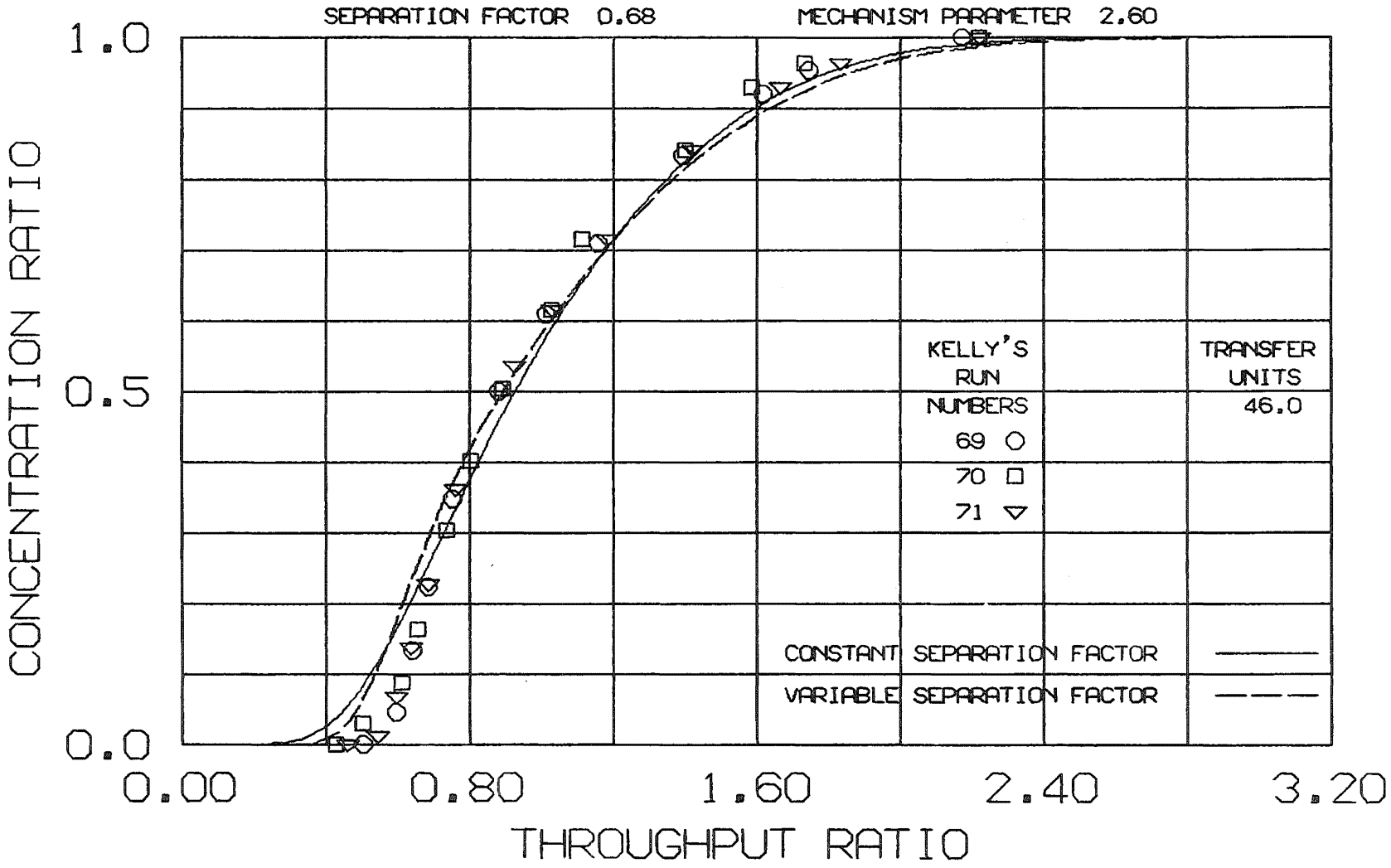
GRAPH 5-15. COMPUTED AND EXPERIMENTAL BREAKTHROUGH CURVES, 1.0 NA-H-CL REGENERATION



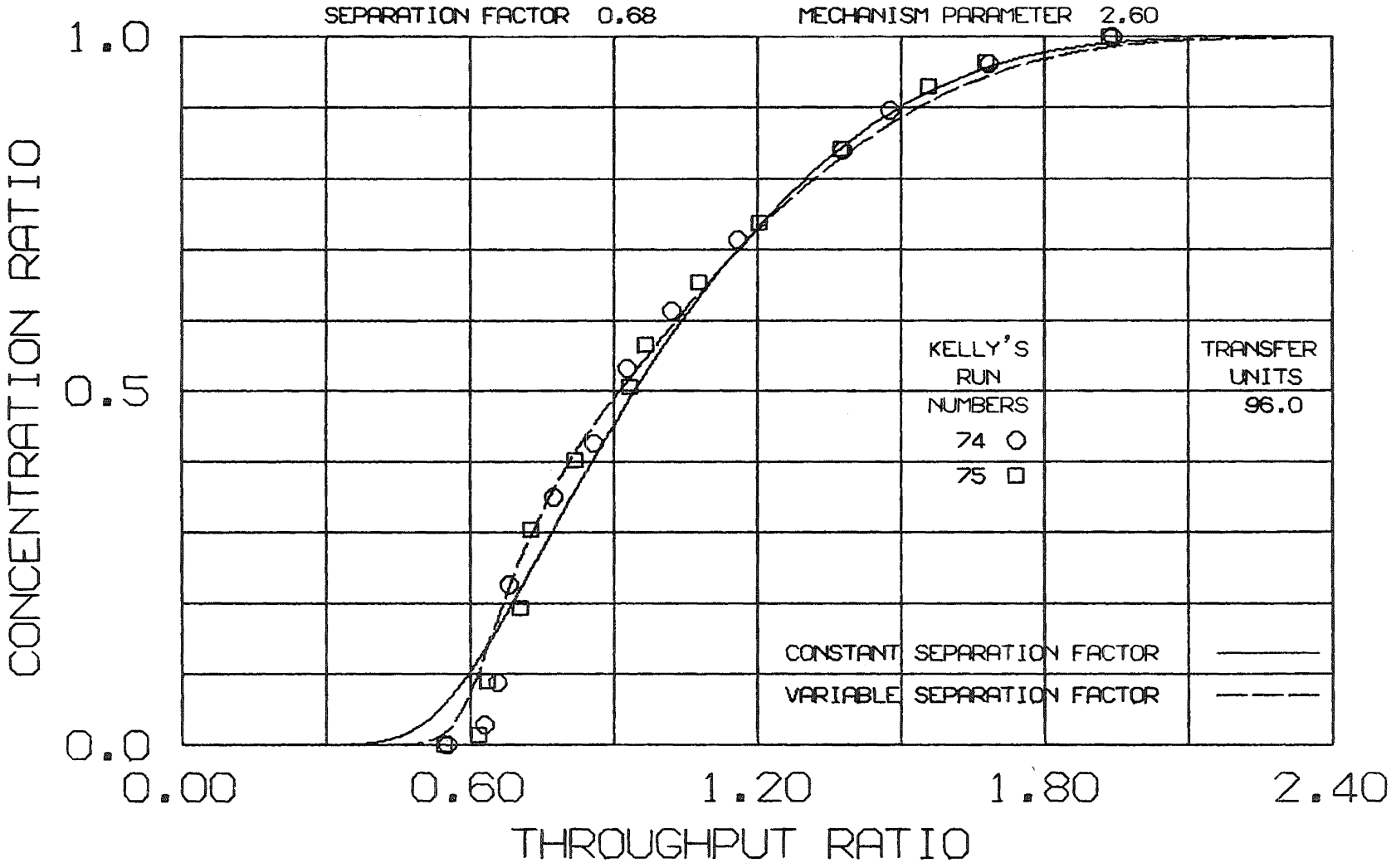
GRAPH 5-16. COMPUTED AND EXPERIMENTAL BREAKTHROUGH CURVES, 1.ON NA-H-CL REGENERATION.



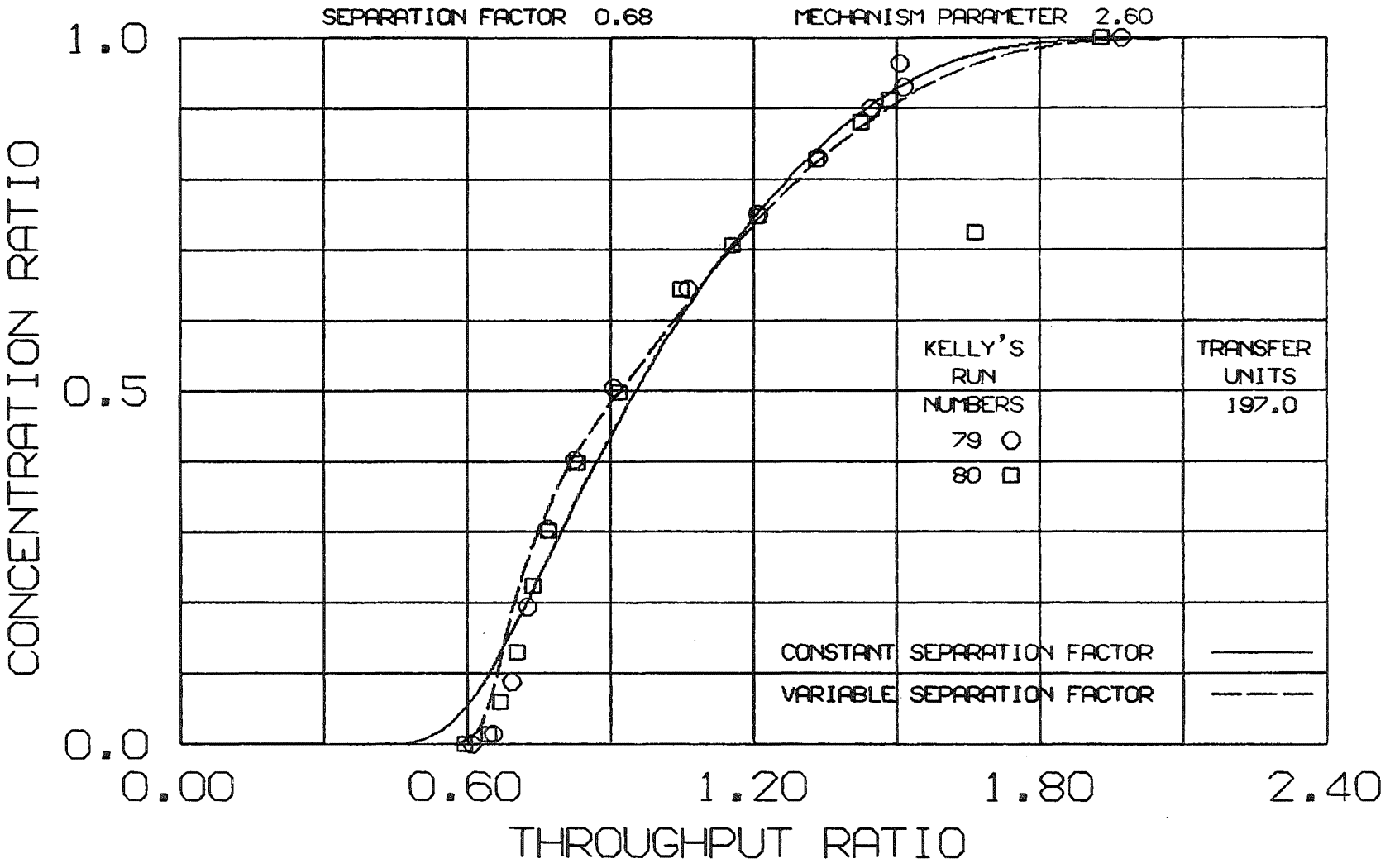
GRAPH 5-17. COMPUTED AND EXPERIMENTAL BREAKTHROUGH CURVES, 0.1N NA-H-CL REGENERATION.



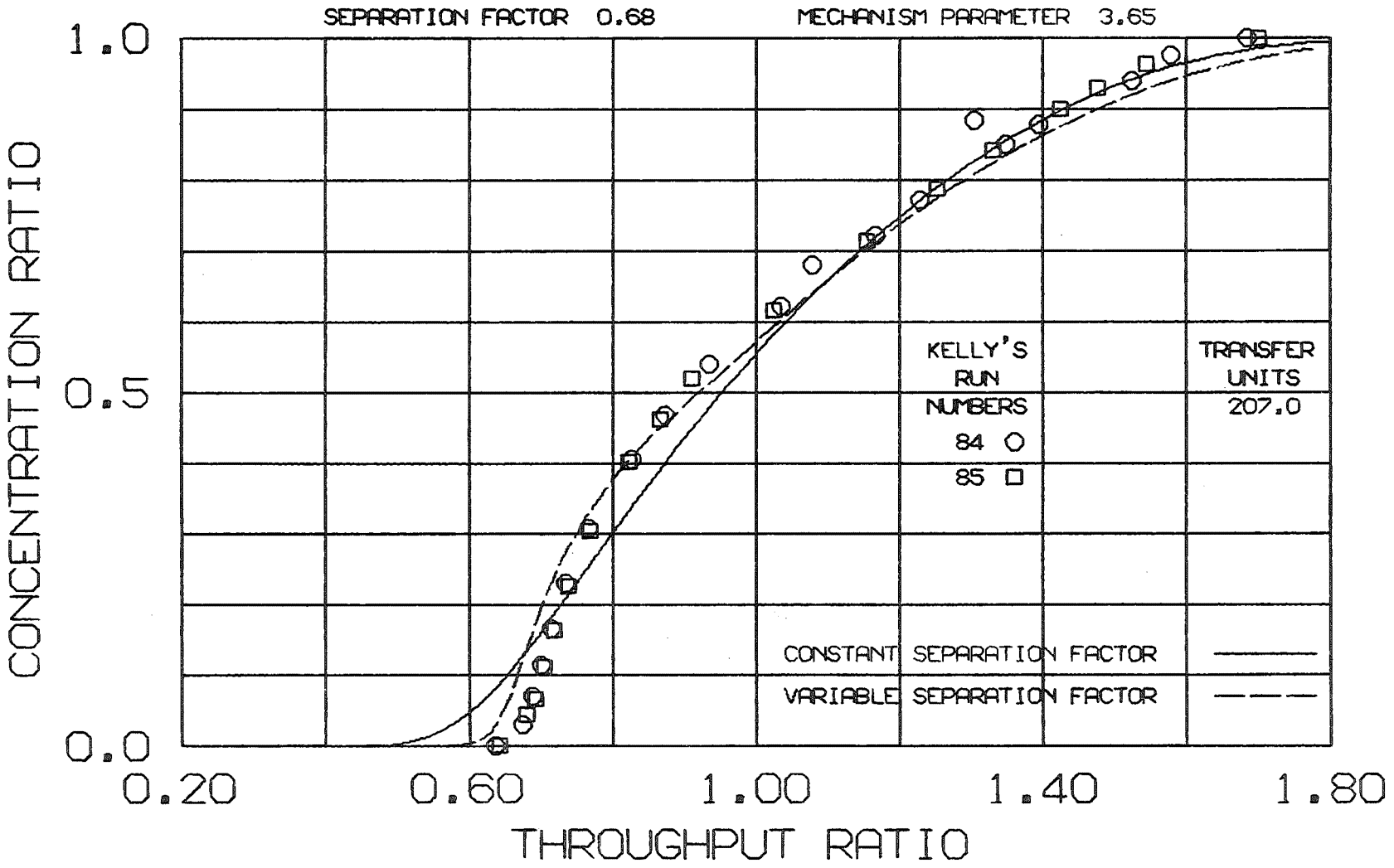
GRAPH 5-18. COMPUTED AND EXPERIMENTAL BREAKTHROUGH CURVES, 0.1N NA-H-CL REGENERATION.



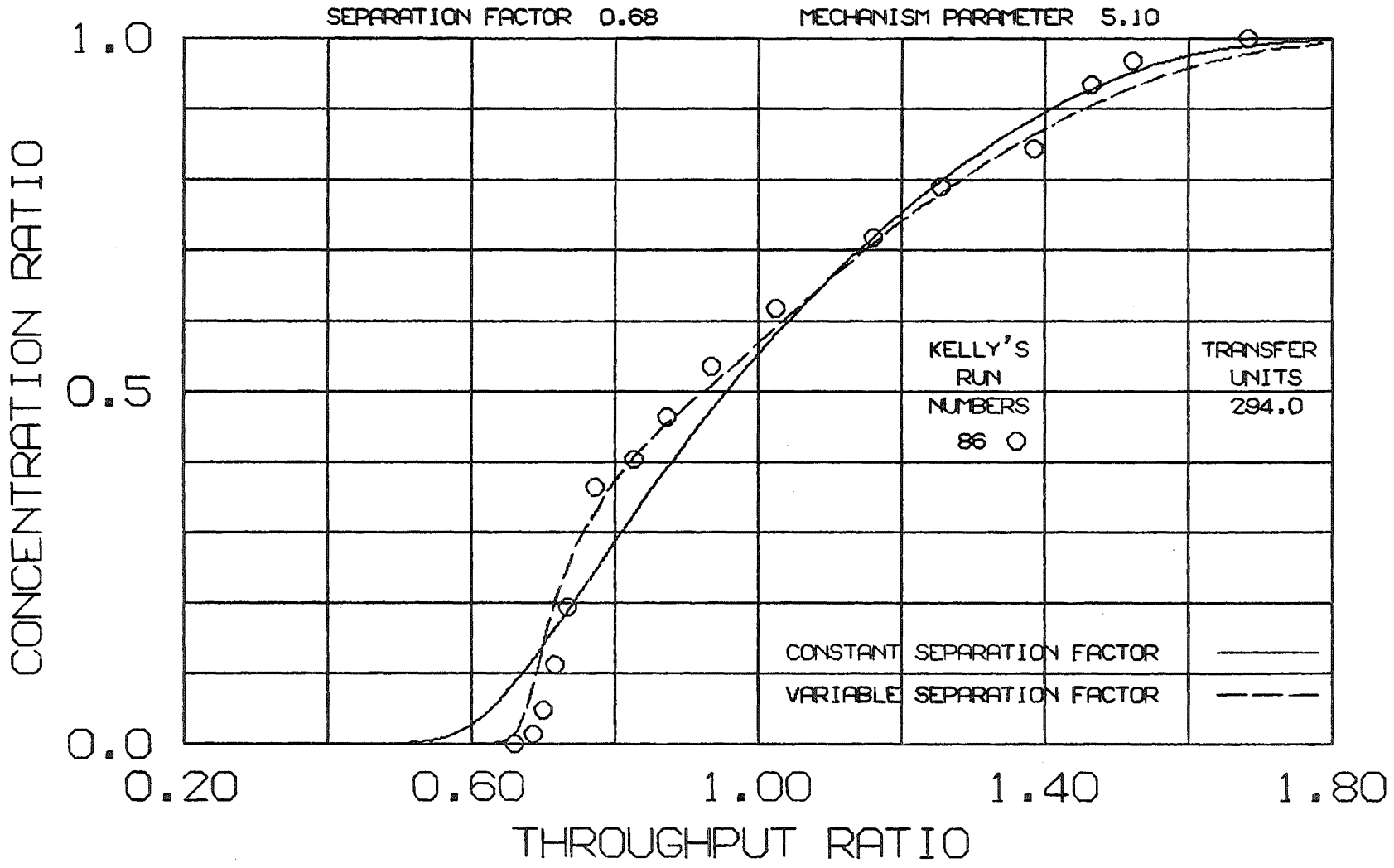
GRAPH 5-19. COMPUTED AND EXPERIMENTAL BREAKTHROUGH CURVES, 0.1N NA-H-CL REGENERATION.



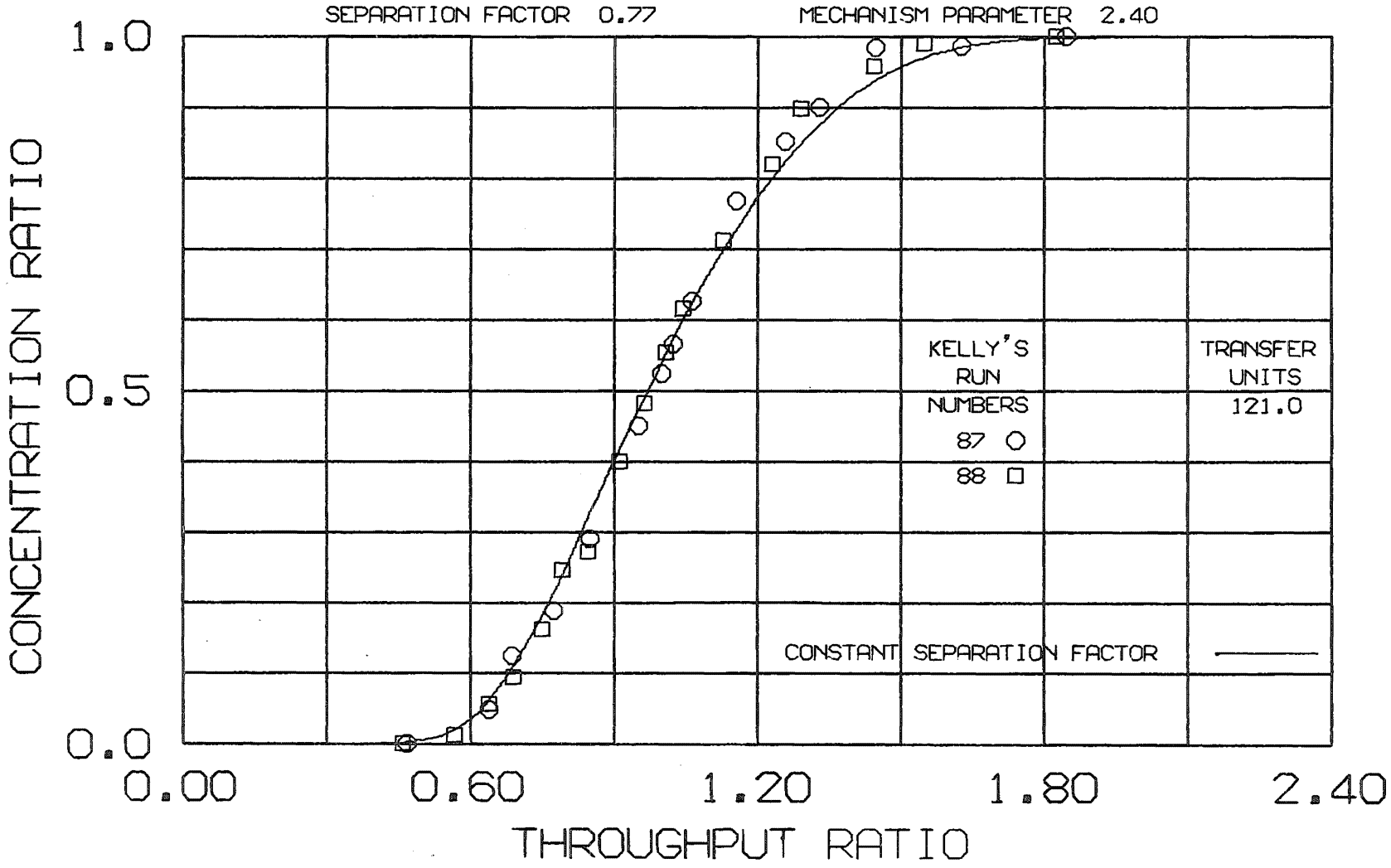
GRAPH 5-20. COMPUTED AND EXPERIMENTAL BREAKTHROUGH CURVES, 0.1N NA-H-CL REGENERATION.



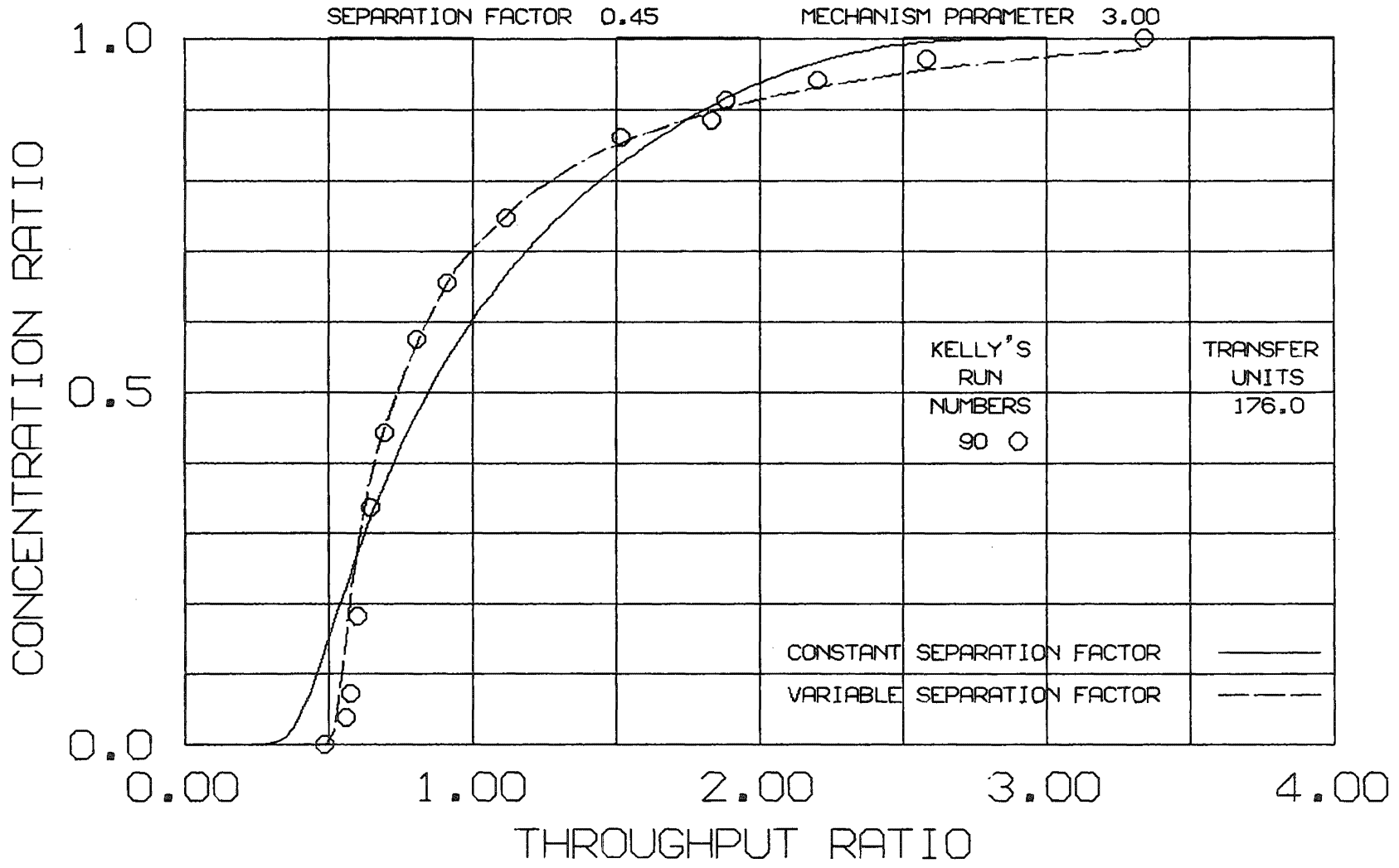
GRAPH 5-21. COMPUTED AND EXPERIMENTAL BREAKTHROUGH CURVES, 0.1N NA-H-CL REGENERATION.



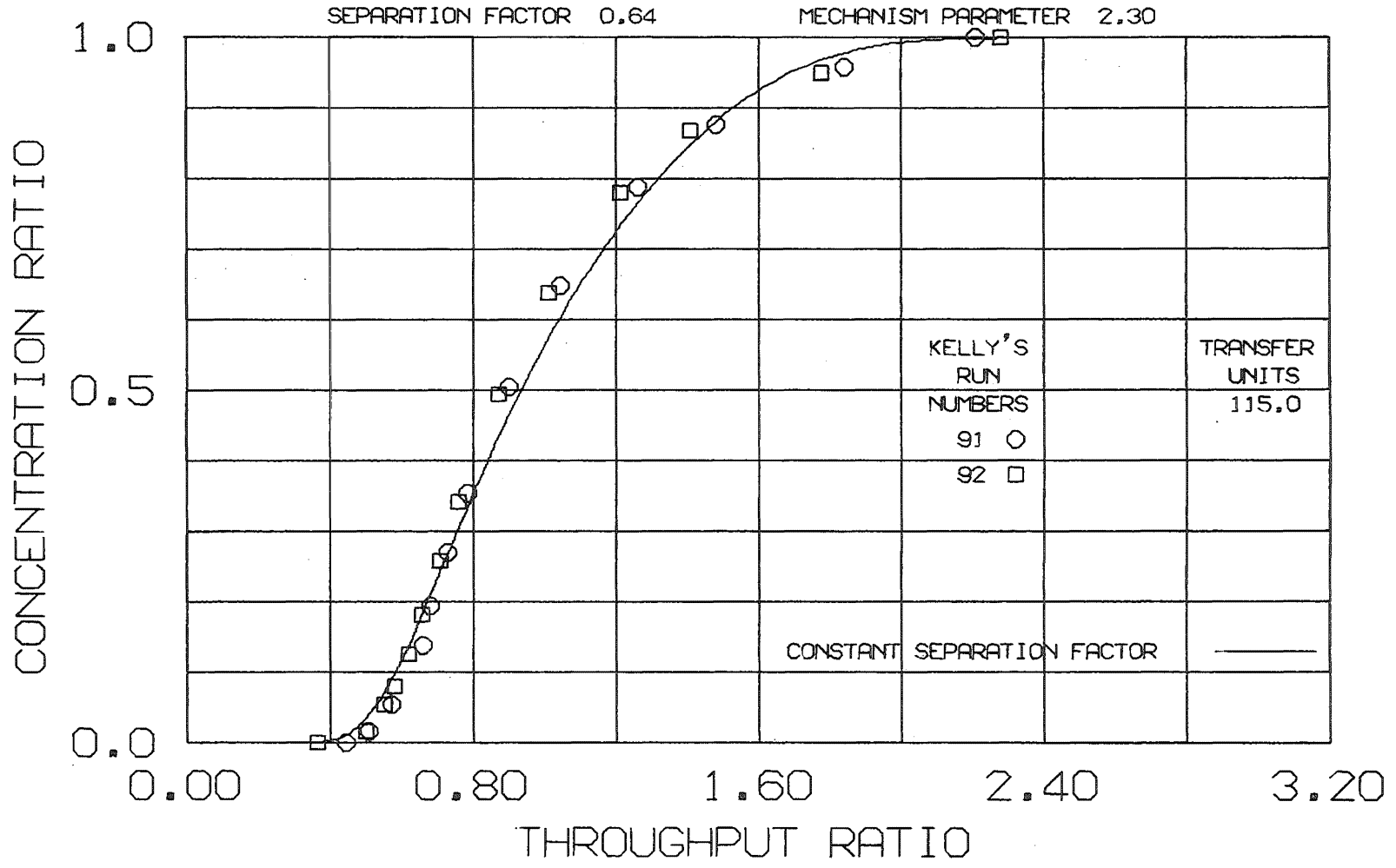
GRAPH 5-22. COMPUTED AND EXPERIMENTAL BREAKTHROUGH CURVES, 0.1N NA-H-CL REGENERATION.



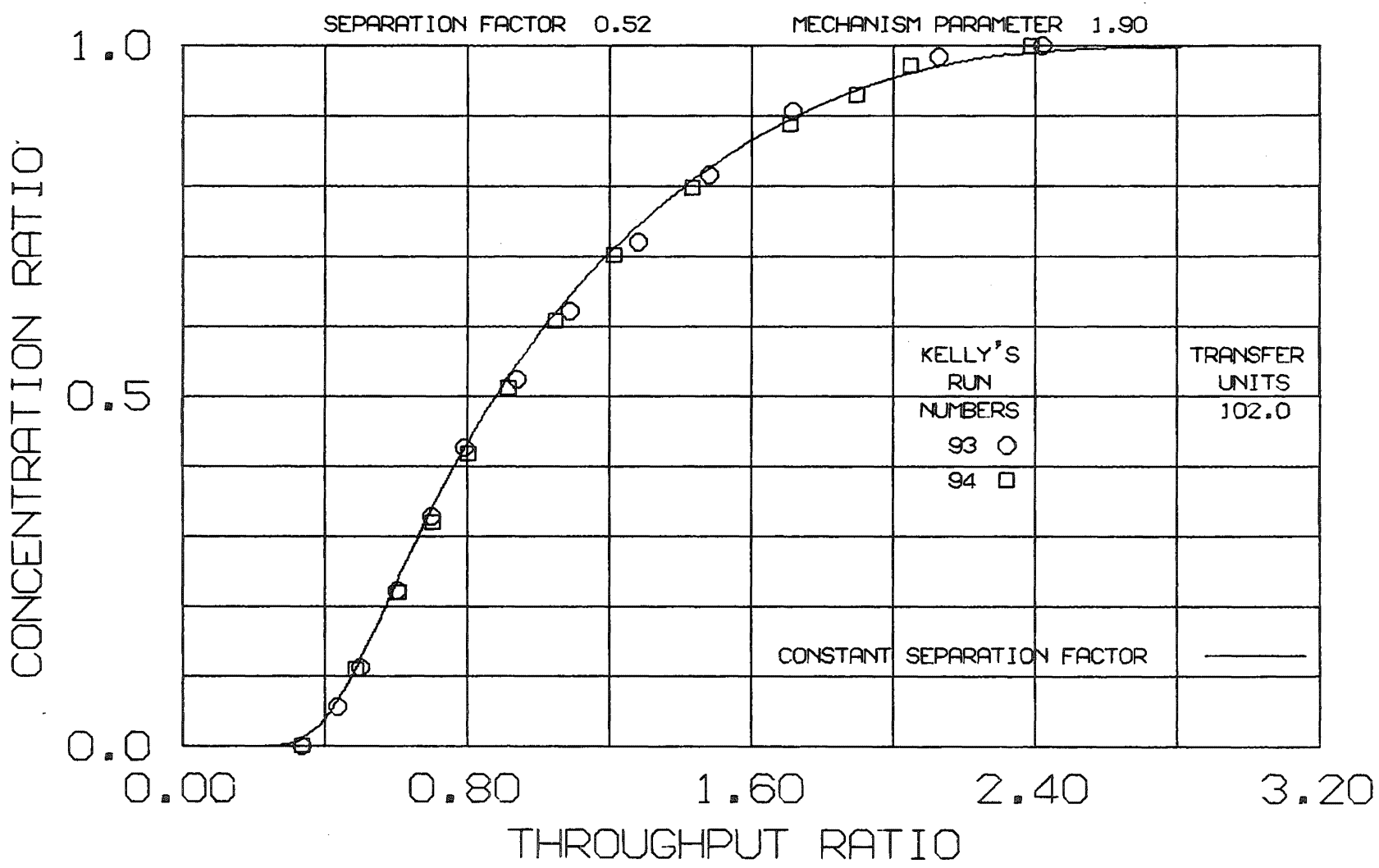
GRAPH 5-23. COMPUTED AND EXPERIMENTAL BREAKTHROUGH CURVES, 0.1N H-LI-CL REGENERATION.



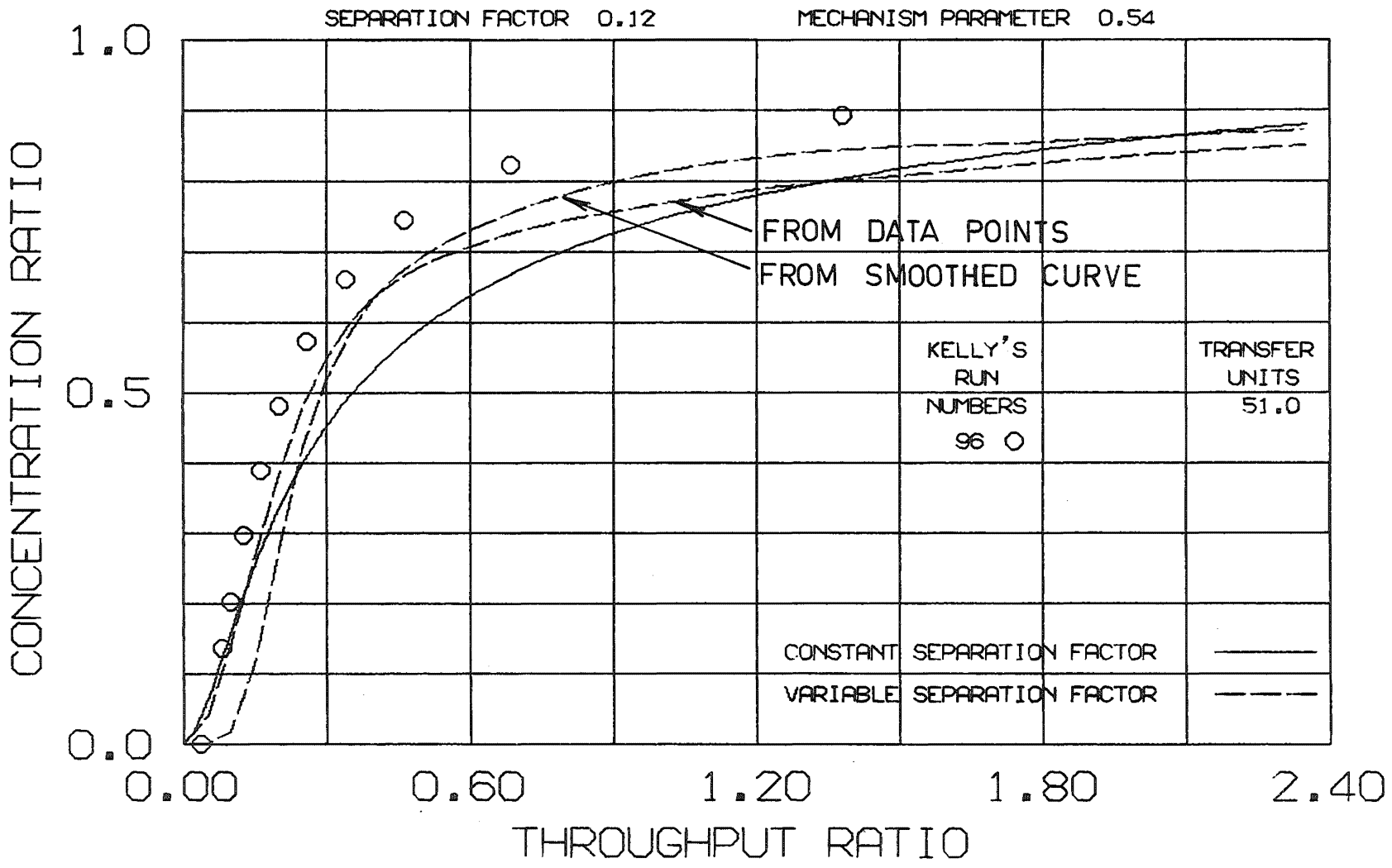
GRAPH 5-24. COMPUTED AND EXPERIMENTAL BREAKTHROUGH CURVES, 0.1N K-H-CL REGENERATION.



GRAPH 5-25. COMPUTED AND EXPERIMENTAL BREAKTHROUGH CURVES, 0.1N K-NA-CL REGENERATION.



GRAPH 5-26. COMPUTED AND EXPERIMENTAL BREAKTHROUGH CURVES, 0.1N NA-LI-CL REGENERATION.



GRAPH 5-27. COMPUTED AND EXPERIMENTAL BREAKTHROUGH CURVES, 0.1N CA-NA-CL REGENERATION.

For the exhaustion runs, equilibrium is favourable and the shape of the breakthrough curve depends more on rate effects - less on equilibrium. This explains the good simulation of exhaustion data by IXLR with a constant separation factor.

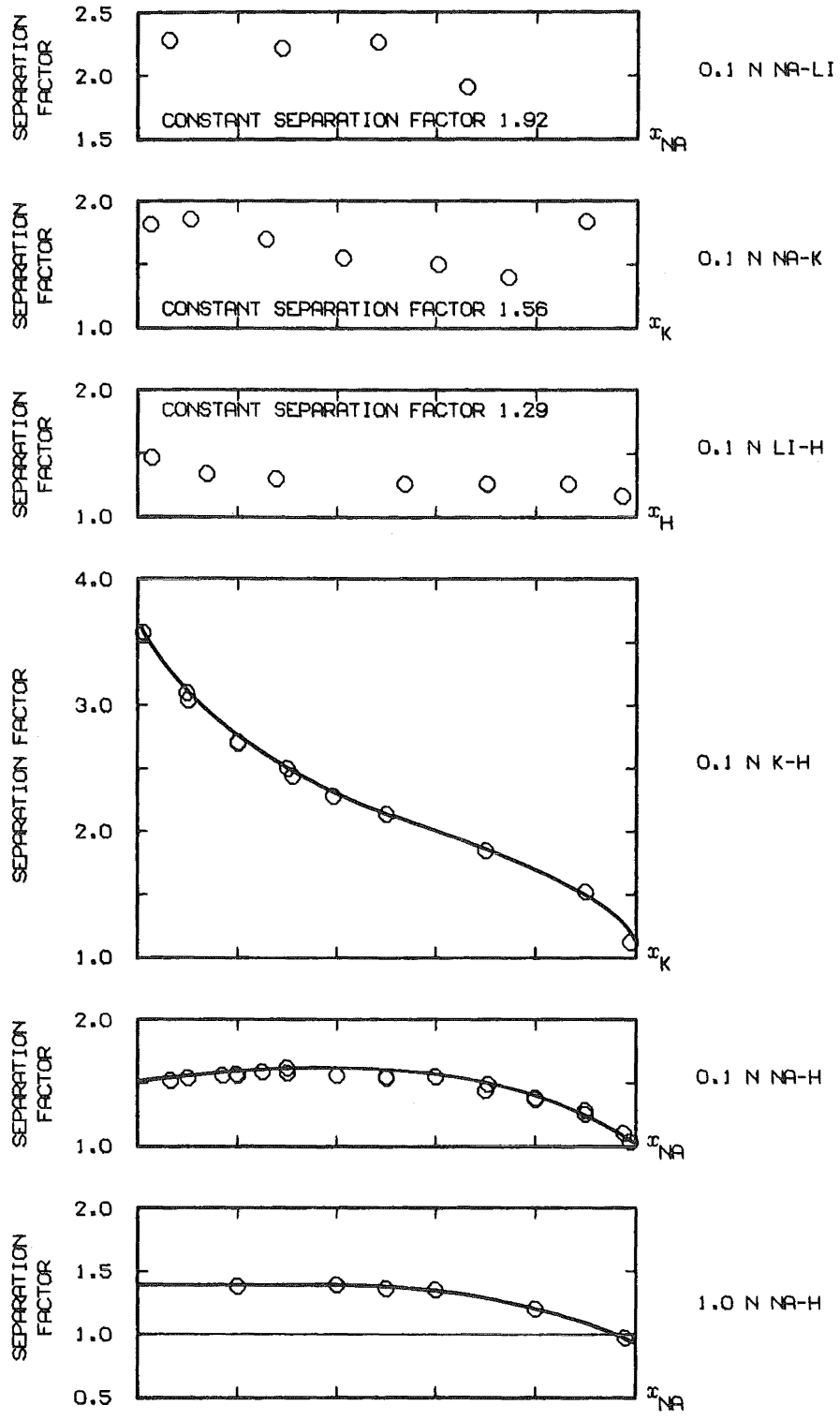
The selectivity concentration dependence of the Ca-Na system is sufficient to merit special consideration. In addition, the system is experimentally difficult, as Graph 5-29 shows, and the selectivity-concentration relation is not well defined. Two have been used; one suggested by Kelly (who calculated K values direct from his data) and the other by drawing a smooth curve through the x*/y* data and then preparing the K/x* data from this. Graph 5-27 shows that either is an improvement on the assumption of a constant separation factor, but that neither really follows the data. Further equilibrium information is needed.

The Ca-Na exhaustion breakthrough curve was recomputed with the variable separation factor modification. (Graph 5-14). The shape is slightly improved, particularly in relation to Run 96 which appears to be displaced to lower values of the throughput ratio. With such favourable equilibrium, the breakthrough curve should be mass-transfer limited and insensitive to equilibrium effects.

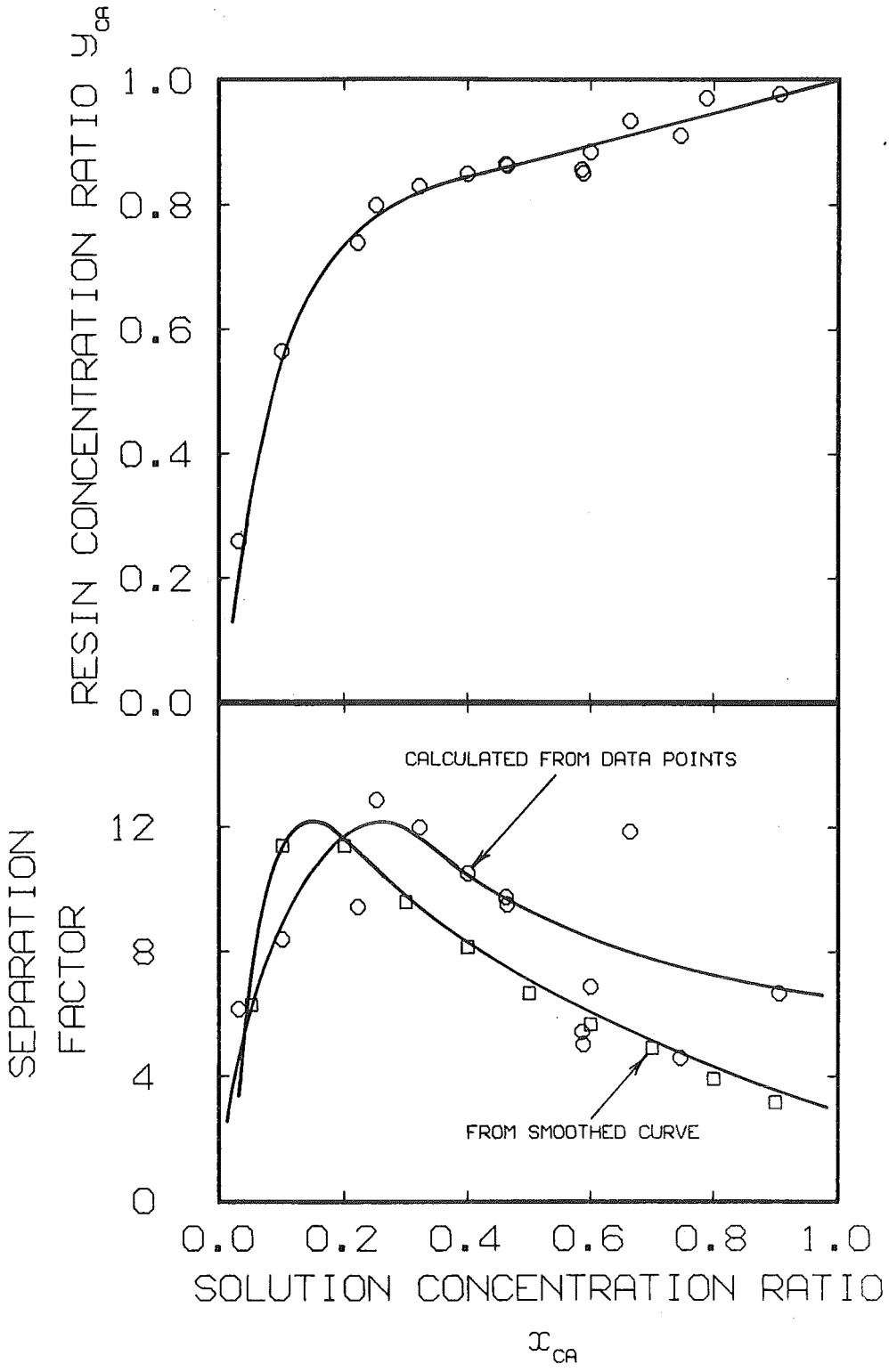
5-7 Modification of IXLR for Concentration-Dependent Separation Factor (IXVK)

The program IXLR is easily modified to allow the separation factor to be a function of concentration. The main program is unchanged except to read in the separation factor/concentration relation. The major modification is to the RATE subprogram, as shown in Figure 5-7.

Iteration is required. A value of x* is guessed and used to calculate the separation factor. The RATE subprogram in its original form, but now called RATEM, is used to calculate $\frac{dy}{dT}$, x* and y*, as Figure 5-4. If the calculated value of x* is the same as the trial values, the iteration has converged and a return can be made to the main program. If not, the Wegstein method (Wegstein, 1958) is used to refine the estimate of x*.



GRAPH 5-28. THE EFFECT OF CONCENTRATION ON SEPARATION FACTOR (KELLY, 1966).



GRAPH 5-29. EQUILIBRIUM EXPRESSION FOR THE CA-NA-CL SYSTEM.

The separation factor is calculated by linear interpolation of 21 equally spaced data points taken from Graphs 5-28 and 5-29. Appendix 5D contains a program listing.

The new program IXVK was tested against IXLR using constant values of the separation factor. Identical results were given for:-

$$N = 10.0,\ 50.0$$

$$\xi = 0.0,\ 1.0,\ 10.0$$

$$K = 0.2,\ 1.0,\ 5.0.$$

In addition, the modified RATE subprogram was checked by hand under a range of conditions with varying selectivity. The same step-sizes were used as in unmodified IXLR.

Graph 5-30 is included as an example to show the effect of the variation in separation factor for a simple case; -

$$K = .5 + 1.0\ x^*$$

$$\xi = 1.0$$

$$N = 50.0$$

and is compared with equivalent conditions but linear equilibrium. The effect of using a non-constant separation factor on matching experimental results has been discussed in the previous section.

The modified program could be used exactly as IXLR, the only noticeable difference was that computing was slower by a factor of 3 or 4, the number of iterations required for convergence.

5-8 General Presentation of Computed Breakthrough Curves

With a program such as IXLR available it should be possible to generate a body of fixed-bed ion exchange breakthrough curves for a range of values of separation factor, mechanism parameter and transfer units. These general breakthrough curves could be used for at least preliminary design when the assumptions of IXLR are reasonable without further (or with minimal) recourse to the computer. It is the purpose of this section to present such a body of results which can be found in Appendix 5E.

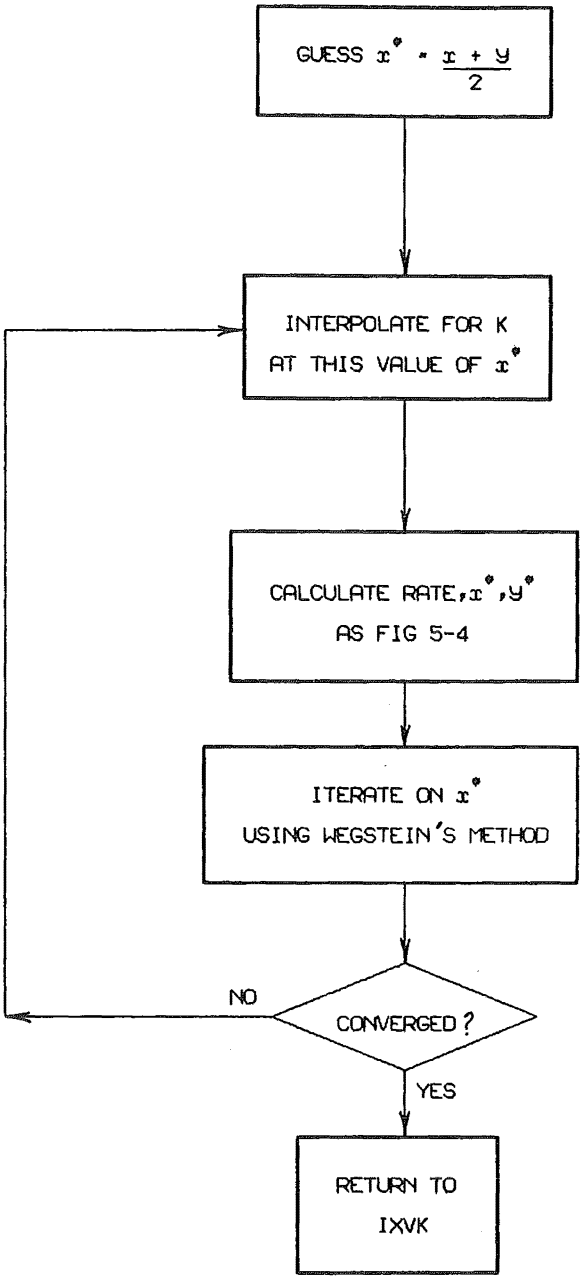
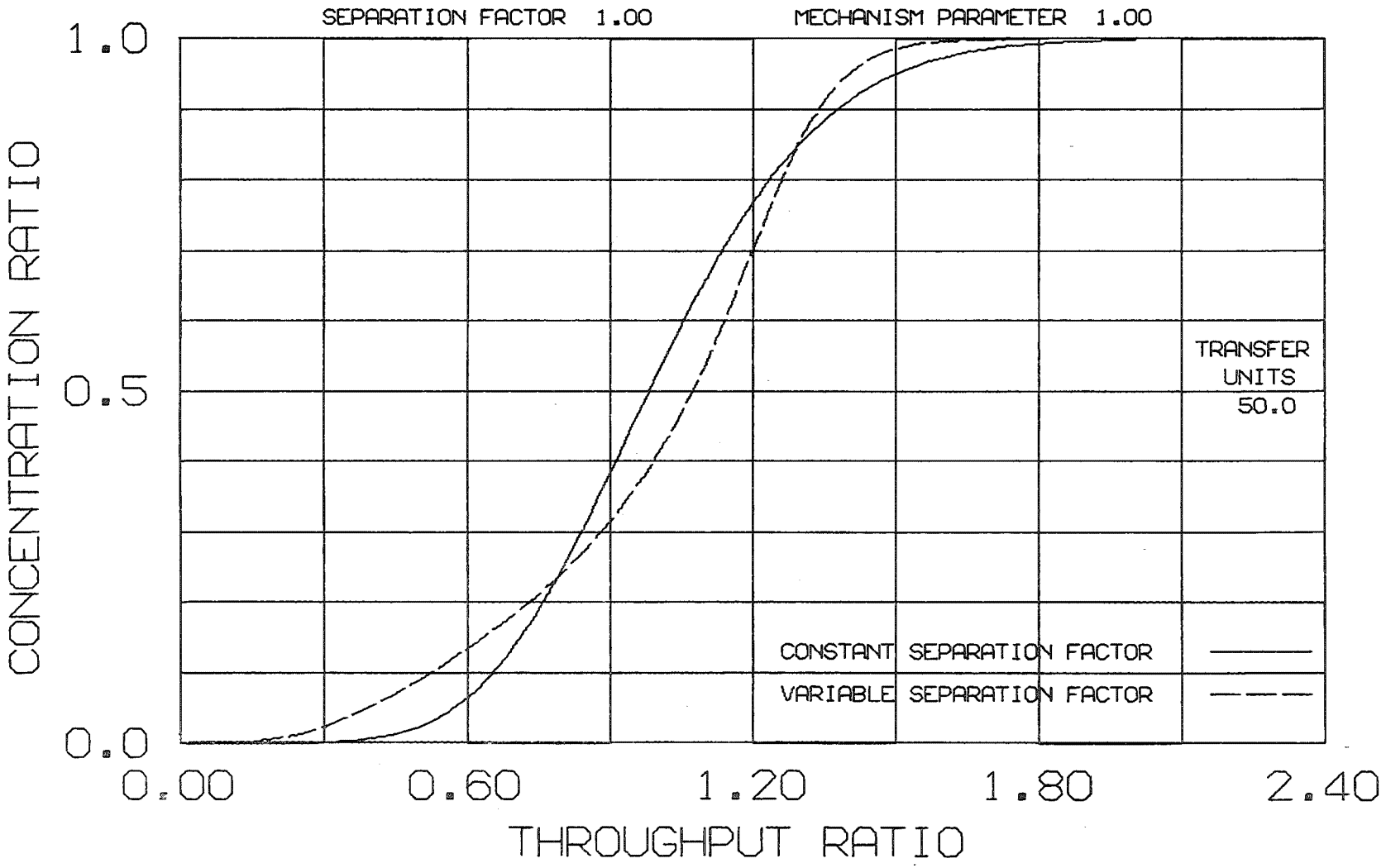


FIGURE 5-7. THE MODIFIED RATE SUBPROGRAM FOR CONCENTRATION-DEPENDENT SELECTIVITY.



GRAPH 5-30. EFFECT OF VARIABLE SEPARATION FACTOR.

Breakthrough curves are listed for all combinations of the parameters:-

K =	0.1	0.5	0.8	1.0	1.2	2.0	10.0			
ξ =	0.0	0.1	0.3	0.5	1.0	2.0	3.0	10.0		
N =	10.0	20.0	30.0	40.0	50.0	60.0	70.0	80.0	90.0	100.0

Each breakthrough curve consists of eleven values of the characteristic time, T, all at the following fixed values of the solution concentration, x:-

x =	0.0	0.0245	0.0955	0.2061	0.3455	0.5
	0.6545	0.7939	0.9045	0.9755	1.0	

or $x = \frac{1.0 - \cos(\frac{i\pi}{10})}{2}$ for i = 0,1,2,··,10

These values were chosen firstly to aid interpolation using Chebyshev polynomials (Goodwin, 1961, page 71) and secondly because the points are then more closely spaced towards x = 0.0 and 1.0 where the curvature is generally greater.

5-9 Conclusions

The program IXLR can compute breakthrough curves for complete exhaustion or regeneration for fixed-bed ion exchange operations which compare well with experimental results. If the separation factor for a system is not constant, then this effect must be included in IXLR.

The computation is based on equilibrium information (best established from independent measurement) and mass transfer rates (standard correlations can be used, Hiester et al., 1956).

The use of the linear particle rate expression has not caused any systematic deviation between IXLR and experimental results.

No stability problem has been found with IXLR for any combination of column parameters. The computing speed is good, particularly for exhaustion, and could be further increased if the accuracy requirements were relaxed.

APPENDIX 5A

The Application of the Method of Characteristics to the Fixed-Bed Ion Exchange Equations.

The equations to be solved are:-

$$\frac{\partial x}{\partial N} + \frac{\partial y}{\partial T} = 0 \qquad (5A\text{-}1)$$

$$\frac{\partial y}{\partial T} = R(x,y) \qquad (5A\text{-}2)$$

where R, the rate function, is obtained from Equations 5-6 and 5-7. Its form does not need to be specified, only that it is a function of x and y.

If the equations for the total differentials are written

$$dx = \frac{\partial x}{\partial N} \cdot dN + \frac{\partial x}{\partial T} \cdot dT$$

$$dy = \frac{\partial y}{\partial N} \cdot dN + \frac{\partial y}{\partial T} \cdot dT$$

then we have a set of 4 equations in the unknowns $\frac{\partial x}{\partial N}$, $\frac{\partial y}{\partial N}$, $\frac{\partial x}{\partial T}$, $\frac{\partial y}{\partial T}$

$$\begin{bmatrix} 1 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 \\ dN & dT & 0 & 0 \\ 0 & 0 & dN & dT \end{bmatrix} \cdot \begin{bmatrix} \partial x/\partial N \\ \partial x/\partial T \\ \partial y/\partial N \\ \partial y/\partial T \end{bmatrix} = \begin{bmatrix} 0 \\ R \\ dx \\ dy \end{bmatrix}$$

The point of the method is to find conditions whereby the partial derivatives can be expressed in terms of the total derivatives. The characteristics are the directions along which this can be done.

A unique and therefore trivial solution (Ames, 1969) will result unless the determinant of the matrix is zero, that is

$$dN \cdot dT = 0$$

This defines the characteristics of the system:-

$$dN = 0 \qquad dT = 0$$

along which the partial differential equation can be replaced by ordinary differential equations.

In this singular case, for any solutions for the partial derivatives to exist, then the other determinants of the system, for example

$$\begin{vmatrix} 1 & 0 & 0 & 1 \\ 0 & 0 & R & 1 \\ dN & dT & dx & 0 \\ 0 & 0 & dy & dT \end{vmatrix}$$

must also be zero, and these conditions give the ordinary differential equations which must be solved along the characteristics:-

$$\frac{dy}{dT} = R \quad \text{along } dN = 0$$

$$\frac{dx}{dN} = -R \quad \text{along } dT = 0$$

These are the equations that IXLR must solve numerically.

APPENDIX 5B

PROGRAM LISTING - IXLR

```
C
C                                IXLR
C
C     ION EXCHANGE MODEL,LINEAR PARTICLE-SIDE RATE EQUATION
C
C   PURPOSE
C
C     TO CALCULATE FIXED-BED ION EXCHANGE COLUMN BREAKTHROUGH CURVES
C     THE EQUATIONS SOLVED ARE
C            DX/DN & DY/DT = 0
C                    DY/DT = R = AMDA * (YSTAR - Y)
C                              = MU * (X - XSTAR)
C
C     NOTE AMDA=SIGMA,MU=RO
C
C     BASIS ON SIDE WITH LESSER NUMBER OF TRANSFER UNITS
C
C
C   USAGE
C
C     READ IN PARAMETERS FOR EACH BREAKTHROUGH CURVE
C         READ(5,100) ZETA,EK,PEND,QEND,DERP,DERQ,NINCP,NINCQ,LPUN
C     100 FORMAT(6E10.4,2I4,L4)
C
C
C   PARAMETERS
C
C     ZETA = MECHANISM PARAMETER
C                  IF ZETA INFINITE,ZETA PUT TO -10.0
C     EK = EQUILIBRIUM RATIO
C     PEND,QEND = GREATEST VALUE OF N,T REQUIRED
C     DERP,DERQ = STEP SIZE IN N,T RESPECTIVELY
C     NINCQ=GOPRIN,THE LOWER VALUE OF N AT WHICH PRINTING SHOULD START
C     NINCP = PRINT INTERVAL IN N IN MULTIPLES OF DERP
C     LPUN = .TRUE. IF RESULTS TO BE PUNCHED
C
C   SUBPROGRAMS REQUIRED
C
C     AREA     NUMERICAL INTEGRATION
C     KLOCK    TIME OF DAY IN SECONDS
C     RATE     RATE FUNCTION
C
0001            COMMON ZETA,EK,RZETA,RZETAP,FAC1,FAC2,AMDA,LINEAR,LIMIT,XSTAR,
               1YSTAR
0002            DIMENSION X(2005),Y(2005),R(2005),Q(2005)
0003            DIMENSION XST(2005),YST(2005)
0004            LOGICAL LPUN,LINEAR,LIMIT
C
C     READ DATA
```

```
                C
0005                1 READ(5,100) ZETA,EK,PEMD,QEND,DERP,DERQ,NINCP,NINCQ,LPUN
0006              100 FORMAT(6E10.4,2I4,L4)
                C
                C     INITIALISATION TO START OF CALCULATION
0007                  WRITE(6,101)
0008              101 FORMAT(1H1,45X,'ION EXCHANGE MODEL IXLR'///)
0009                  IF(LPUN)WRITE(7,110)ZETA,EK,PEND,QEND,DERP,DERQ,NINCP,NINCQ
0010              110 FORMAT('99900 ION EXCHANGE MODEL IXLR'/
                   1'99901'6F10.5,2I4,L4)
0011                  IP=1
0012                  NP=PEMD/DERP+1
0013                  NQ=QEND/DERQ+1
0014                  IGO=1
0015                  NLEV=0
0016                  NQP1=NQ+1
0017                  NPP1=NP+1
0018                  IF(NPP1.LE.2005.AND.NPQ1.LE.2005)GOTO47
0019                  WRITE(6,133)NPP1,NPQ1
0020              133 FORMAT('0TOO MANY POINTS '2I7)
0021                  GOTO1
0022               47 IXTIME=KLOCK(3)
0023                  GOPRIN=NINCQ
0024                  WRITE(6,102) ZETA,EK,DERP,DERQ
0025              102 FORMAT(' MECHANISM PARAMETER =',G12.5/' EQUILIBRIUM RATIO =',G12.5
                   1/' STEP SIZE IN N =',G12.5/' STEP SIZE IN T =',G12.5,60X,G10.4)
                C
                C     DECISION ON BASIS
0026                  IF(ZETA-1.0002)50,50,51
                C
                C     PARTICLE PHASE BASIS
0027               50 AMDA=1.0
0028                  WRITE(6,126)
0029              126 FORMAT(' N AND T(IE ZN) ARE BASED ON NUMBER OF PARTICLE PHASE TRAN
                   1SFER UNITS')
0030                  GO TO 52
                C
                C     SOLUTION PHASE BASIS
0031               51 AMDA=ZETA
0032                  WRITE(6,107)
0033              107 FORMAT(' N AND T(IE ZN) ARE BASED ON NUMBER OF SOLUTION PHASE TRAN
                   1SFER UNITS')
                C
                C     SET UP COMMON VARIABLES FOR USE IN RATE FUNCTION
0034               52 RZETA=1.0/ZETA
0035                  LIMIT=.FALSE.
0036                  IF(ZETA.LT.0.0001)LIMIT=.TRUE.
0037                  IF(EK.LT.0.9998.OR.EK.GT.1.0002) GO TO 56
                C
```

```
                C     LINEAR EQUILIBRIUM
0038                  FAC1=1.0
0039                  FAC2=1.0
0040                  LINEAR=.TRUE.
0041                  GO TO 57
                C     NON LINEAR EQUILIBRIUM
0042             56   FAC2=ZETA*(EK-1.0)
0043                  FAC1=(1.0+EK*ZETA)/FAC2
0044                  FAC2=EK/FAC2
0045                  LINEAR=.FALSE.
0046             57   RZETAP=1.0/(ZETA+1.0)
                C                                                  )5,ADMA,ATEZ(PMUDP LLAC
                C
                C     CALCULATION ALONG IP=1
                C
0047                  X(1)=1.0
0048                  Y(1)=0.0
0049                  R(1)=RATE(1.0,0.0)
0050                  Q(1)=0.0
0051                  INIL=1
0052                  DO200IQ=2,NQP1
0053                  XD=IQ
0054                  Q(IQ)=(XD-1.0)*DERQ
0055                  X(IQ)=1.0
                C
                C     CHECK THAT Y NOT 1.0
0056                  IF(Y(IQ-1).LE.0.9999) GO TO 17
0057                  Y(IQ)=1.0
0058                  R(IQ)=0.0
0059                  GO TO 200
                C
                C     RUNGE KUTTA PROCEDURE TO GET Y(IQ), NOTE X(IQ)=1.0
0060             17   YO=Y(IQ-1)
0061                  RKO=DERQ*R(IQ-1)
0062                  XD=YO+.5*RKO
0063                  RK1=DERQ*RATE(1.0,XD)
0064                  XD=YO+RK1*.5
0065                  RK2=DERQ*RATE(1.0,XD)
0066                  XD=YO+RK2
0067                  RK3=DERQ*RATE(1.0,XD)
0068                  Y1=YO+(RKO+2.0*(RK1+RK2)+RK3)/6.0
0069                  Y(IQ)=Y1
0070                  R(IQ)=RATE(1.0,Y1)
0071                  ISAT=IQ
                C                                QI,PI,)QI(R,1Y,3KR,2KR,1KR,OKR,OY)171,6(ETIRW
0072             171  FORMAT(9G14.5)
0073             200  CONTINUE
                C
                C     NOW SUCCESSIVE INCREMENTATION DOWN COLUMN
```

```
      C
0074        DO204IP=2,NPP1
0075        IF(INIL.NE.1) GO TO 12
      C
      C     INIL=1, CALCULATION OF X(1), NOTE Y(1)=0.0, USING RUNGE KUTTA
0076        X0=X(1)
0077        RK0=-DERP*R(1)
0078        XD=X0+RK0*.5
0079        RK1=-DERP*RATE(XD,0.0)
0080        XD=X0+RK1*.5
0081        RK2=-DERP*RATE(XD,0.0)
0082        XD=X0+RK2
0083        RK3=-DERP*RATE(XD,0.0)
0084        X1=X0+(RK0+RK3+2.0*(RK1+RK2))/6.0
0085        X(1)=X1
0086        R(1)=RATE(X1,0.0)
0087        XST(1)=XSTAR
0088        YST(1)=YSTAR
0089        JSAT=2
0090        IF(IP.LT. 5.AND.IQ.LT.3)WRITE(6,171)X0,RK0,RK1,RK2,RK3,X1,R(1),IP,     C
           1IQ                                                                     C
0091        GO TO 6
      C
      C     CALCULATION OF OTHER X,Y AT THIS LEVEL OF P
0092     12 JSAT=INIL
0093      6 DO201IQ=JSAT,NQP1
0094        X1=X(IQ-1)
0095        Y1=Y(IQ-1)
0096        R1=R(IQ-1)
0097        X2=X(IQ)
0098        Y2=Y(IQ)
0099        R2=R(IQ)
      C
      C     CALCULATE FIRST ESTIMATES OF X,Y AT NEW POINT
0100        XD=X2-R2*DERP
0101        YD=Y1+R1*DERQ
      C
      C     CHECK THAT X,Y NOT LESS THAN .0001
0102        IF(XD+YD.GT.0.0001) GO TO 21
      C     COLUMN STILL EMPTY
0103        X(IQ)=0.0
0104        Y(IQ)=0.0
0105        R(IQ)=0.0
0106        XST(IQ)=0.0
0107        YST(IQ)=0.0
0108        INIL=IQ
0109        GOTO201
      C
      C     CHECK THAT X,Y NOT GREATER THAN .9999
```

```
0110            21 IF(XD+YD.LT.1.9999) GO TO 22
                C     COLUMN SATURATED, BRANCH OUT OF LOOP
0111                  X(IQ)=1.0
0112                  Y(IQ)=1.0
0113                  R(IQ)=0.0
0114                  XST(IQ)=1.0
0115                  YST(IQ)=1.0
0116                  ISAT=IQ
0117                  GOTO13
                C
                C     CALCULATION OF SECOND ESTIMATES OF X,Y AT THIS POINT
0118            22 RD=RATE(XD,YD)
0119                  XDD=X2-RD*DERP
0120                  YDD=Y1+RD*DERQ
                C
                C     CALCULATION OF FINAL VALUES OF X,Y AT THIS POINT
0121                  X2=0.5*(XD+XDD)
0122                  X(IQ)=X2
0123                  Y2=0.5*(YD+YDD)
0124                  Y(IQ)=Y2
0125                  R(IQ)=RATE(X2,Y2)
0126                  XST(IQ)=XSTAR
0127                  YST(IQ)=YSTAR
                C
                C     CHECK X IN ACCEPTABLE RANGE
0128                  IF(ABS(X2-.5).LE.0.501)GOTO201
                C     X OUTSIDE RANGE
0129                  WRITE(6,108)
0130            108 FORMAT(' SOLUTION CONCENTRATION NOT IN ACCEPTABLE RANGE')
0131                  NAMELIST/XOUT/IP,IQ,X,Y,R
0132                  WRITE(6,XOUT)
0133                  GO TO 59
0134            201 CONTINUE
                C
                C     PRINTOUT OF BREAKTHROUGH CURVES
0135             13 NLEV=NLEV+1
0136                  IF(NLEV.LT.NINCP) GO TO 204
0137                  NLEV=0
0138                  P=IP-1
0139                  P=P*DERP
0140                  IF(P.LT.GOPRIN)GOTO204
0141                  WRITE(6,103) P
0142            103 FORMAT(1H1,'NUMBER OF TRANSFER UNITS =',G12.5/)
0143                  WRITE(6,104)
0144            104 FORMAT(3(6X'T'4X'X'6X'Y'4X'XSTAR YSTAR  RATE'))
0145                  NINCQ=(ISAT-IGO+50)/100
0146                  IF(NINCQ.EQ.0)NINCQ=1
0147                  IGO=INIL/NINCQ*NINCQ+1
0148                  WRITE(6,105)(Q(K),X(K),Y(K),XST(K),YST(K),R(K),K=IGO,ISAT,NINCQ)
```

```
0149          105 FORMAT(3(F8.2,2F7.4,3F6.3))
0150              IOUT=(ISAT-IGO)/NINCQ+1
0151              IF(LPUN)WRITE(7,111)P,IOUT
0152          111 FORMAT('99902'F10.4,I4)
0153              IF(LPUN)WRITE(7,112) (Q(K),X(K),Y(K),K=IGO,ISAT,NINCQ)
0154          112 FORMAT(('99999',5(F5.1,2F5.3)))
0155              IF(ISAT.GT.NQ)GOTO204
0156              DO210IQ=1,ISAT
0157              XST(IQ)=1.0-X(IQ)
0158          210 CONTINUE
0159              RR=AREA(XST,ISAT,DERQ)
0160              WRITE(6,127)RR
0161          127 FORMAT('0AREA'G15.5)
0162          204 CONTINUE
0163              IXTIME=KLOCK(3)-IXTIME
0164              WRITE(6,134) IXTIME
0165          134 FORMAT(////G10.4)
0166           59 GOTO1
0167              END
```

```
0001            FUNCTION RATE(X,Y)
                C
                C   PURPOSE
                C
                C     TO CALCULATE RATE=DY/DT FOR IXLR
                C
                C   USAGE
                C
                C     R=RATE(X,Y)
                C
                C   PARAMETERS
                C
                C     R       THE CALCULATED RATE
                C     X       SOLUTION CONCENTRATION RATIO
                C     Y       AVERAGE PARTICLE CONCENTRATION
                C
                C    MODEL VARIABLES
                C
                C     XSTAR,YSTAR INTERFACIAL EQUILIBRIUM CONCENTRATIONS
                C     ZETA        MECHANISM PARAMETER,NP/NF
                C     K           SEPARATION FACTOR
                C
                C    CALCULATION VARIABLES,SET UP IN IXLR FOR REPEATED USE
                C
                C
                C     RZETA       1.0/ZETA
                C     RZETAP      1.0/(ZETA+1.0)
                C     FAC1        (1.0+K*ZETA)/ZETA/(K-1.0)
                C     FAC2        K/ZETA/(K-1.0)
                C     LINEAR      LOGICAL,TRUE IF LINEAR EQUILIBRIUM
                C     LIMIT       LOGICAL,TRUE IF FILM OR PARTICLE CONTROL
                C
                C     SIGMA=ZETA IF FILM CONTROL
                C           =1.0 IF PARTICLE CONTROL
                C     PUT FAC1,FAC2=1.0 IF K=1.0
                C
                C
0002            REAL K
0003            LOGICAL LINEAR,LIMIT
0004            COMMON ZETA,K,RZETA,RZETAP,FAC1,FAC2,SIGMA,LINEAR,LIMIT,XSTAR,YSTA
                1R
                C
0005            EQX(P)=P/(P+K*(1.-P))
                C
0006            ALFA=X+ZETA*Y
0007            IF(.NOT.LIMIT) GO TO 2
                C
                C     FILM OR PARTICLE CONTROL,ZETA=-10.0 OR 0.0,DECIDE WHICH
                C
```

```
0008              IF(ZETA.LT.-5.0) GO TO 3
                  C
                  C     PARTICLE CONTROL,ZETA=0.0
                  C
0009              YSTAR=K*X/(1.0+(K-1.0)*X)
0010              XSTAR=X
0011              RATE=YSTAR-Y
0012              RETURN
                  C
                  C     FILM CONTROL,ZETA=-10.0,I.E. INFINITY
                  C
0013            3 XSTAR=EQX(Y)
0014              YSTAR=Y
0015              RATE=X-XSTAR
0016              RETURN
                  C
                  C     MIXED DIFFUSION RESISTANCE,TEST FOR LINEAR EQUILIBRIUM
                  C
0017            2 IF(LINEAR) GO TO 6
                  C
                  C     NON-LINEAR EQUILIBRIUM,CALCULATE YSTAR FROM QUADRATIC EQUATION
                  C
0018              B=-(ALFA*RZETA+FAC1)
0019              C=ALFA*FAC2
0020              PAR=-B/2.0
0021              DIS=SQRT(B*B-4.0*C)/2.0
0022              ROOT1=PAR+DIS
0023              IF(PAR.LT.0.0) ROOT1=PAR-DIS
0024              ROOT2=C/ROOT1
0025              E1=ABS(0.5-ROOT1)
0026              E2=ABS(0.5-ROOT2)
0027              YSTAR=ROOT1
0028              IF(E2.LT.E1) YSTAR=ROOT2
                  C
                  C     CALCULATE XSTAR AND RATE
                  C
0029            7 XSTAR=EQX(YSTAR)
0030              RATE=SIGMA*(YSTAR-Y)
0031              RETURN
                  C
                  C     LINEAR EQUILIBRIUM,MIXED DIFFUSION
                  C
0032            6 YSTAR=ALFA*RZETAP
0033              GO TO 7
0034              END
```

```
0001              FUNCTION AREA(X,N,H)
                  C
                  C   PURPOSE
                  C
                  C     THIS SUBPROGRAM EVALUATES THE AREA UNDER THE
                  C          CURVE SAMPLED IN X BY SIMPSON'S RULE
                  C
                  C   USAGE
                  C     AUC=AREA(X,N,H)
                  C
                  C   PARAMETERS
                  C
                  C     AUC AREA UNDER CURVE
                  C     X VECTOR OF ORDINATES, SPACED H APART
                  C     N NUMBER OF ORDINATES
                  C               IF N EVEN,LAST ELEMENT INCLUDED BY TRAPEZOIDAL RULE
                  C
0002              DIMENSION X(1)
                  C
                  C     TEST FOR N EVEN
                  C
0003              IF(N/2*2.EQ.N)GOTO3
                  C   N ODD
0004              SUM=0.0
0005              GOTO4
                  C   N EVEN
0006              3 SUM=(X(N-1)+X(N))/2.0
0007              N=N-1
0008              4 SUM=SUM+X(1)+X(N)
0009              M=N-1
0010              DO 200 I=2,M
                  C
                  C     IF I IS EVEN, FAC=4., OTHERWISE 2.0
                  C
0011              FAC=2.0
0012              IF(I/2*2.EQ.I)FAC=4.0
0013              SUM=SUM+FAC*X(I)
0014            200 CONTINUE
0015              AREA=H/3.0*SUM
0016              RETURN
0017              END
```

ION EXCHANGE MODEL IXLR

MECHANISM PARAMETER = 1.0000
EQUILIBRIUM RATIO = 1.0000
STEP SIZE IN N = 0.25000
STEP SIZE IN T = 0.50000
N AND T(IE ZN) ARE BASED ON NUMBER OF PARTICLE PHASE TRANSFER UNITS

NUMBER OF TRANSFER UNITS = 10.000

T	X	Y	XSTAR	YSTAR	RATE	T	X	Y	XSTAR	YSTAR	RATE	T	X	Y	XSTAR	YSTAR	RATE
0.50	0.0161	0.0026	0.009	0.009	0.007	1.00	0.0293	0.0072	0.018	0.018	0.011	1.50	0.0457	0.0141	0.030	0.030	0.016
2.00	0.0651	0.0234	0.044	0.044	0.021	2.50	0.0874	0.0353	0.061	0.061	0.026	3.00	0.1122	0.0498	0.081	0.081	0.031
3.50	0.1394	0.0668	0.103	0.103	0.036	4.00	0.1685	0.0863	0.127	0.127	0.041	4.50	0.1994	0.1081	0.154	0.154	0.046
5.00	0.2315	0.1321	0.182	0.182	0.050	5.50	0.2647	0.1579	0.211	0.211	0.053	6.00	0.2986	0.1855	0.242	0.242	0.057
6.50	0.3329	0.2145	0.274	0.274	0.059	7.00	0.3673	0.2447	0.306	0.306	0.061	7.50	0.4016	0.2758	0.339	0.339	0.063
8.00	0.4356	0.3075	0.372	0.372	0.064	8.50	0.4690	0.3397	0.404	0.404	0.065	9.00	0.5017	0.3721	0.437	0.437	0.065
9.50	0.5335	0.4044	0.469	0.469	0.065	10.00	0.5644	0.4365	0.500	0.500	0.064	10.50	0.5941	0.4682	0.531	0.531	0.063
11.00	0.6226	0.4993	0.561	0.561	0.062	11.50	0.6499	0.5297	0.590	0.590	0.060	12.00	0.6758	0.5592	0.618	0.618	0.058
12.50	0.7005	0.5878	0.644	0.644	0.056	13.00	0.7238	0.6154	0.670	0.670	0.054	13.50	0.7458	0.6419	0.694	0.694	0.052
14.00	0.7664	0.6672	0.717	0.717	0.050	14.50	0.7858	0.6913	0.739	0.739	0.047	15.00	0.8039	0.7143	0.759	0.759	0.045
15.50	0.8208	0.7360	0.778	0.778	0.042	16.00	0.8364	0.7565	0.796	0.796	0.040	16.50	0.8510	0.7758	0.813	0.813	0.038
17.00	0.8644	0.7940	0.829	0.829	0.035	17.50	0.8769	0.8109	0.844	0.844	0.033	18.00	0.8883	0.8268	0.858	0.858	0.031
18.50	0.8988	0.8416	0.870	0.870	0.029	19.00	0.9085	0.8553	0.882	0.882	0.027	19.50	0.9174	0.8681	0.893	0.893	0.025
20.00	0.9255	0.8799	0.903	0.903	0.023	20.50	0.9328	0.8908	0.912	0.912	0.021	21.00	0.9396	0.9008	0.920	0.920	0.019
21.50	0.9457	0.9101	0.928	0.928	0.018	22.00	0.9513	0.9186	0.935	0.935	0.016	22.50	0.9563	0.9264	0.941	0.941	0.015
23.00	0.9609	0.9335	0.947	0.947	0.014	23.50	0.9650	0.9400	0.952	0.952	0.012	24.00	0.9687	0.9459	0.957	0.957	0.011
24.50	0.9721	0.9514	0.962	0.962	0.010	25.00	0.9751	0.9563	0.966	0.966	0.009	25.50	0.9778	0.9607	0.969	0.969	0.009
26.00	0.9802	0.9648	0.973	0.973	0.008	26.50	0.9824	0.9684	0.975	0.975	0.007	27.00	0.9844	0.9718	0.978	0.978	0.006
27.50	0.9862	0.9747	0.980	0.980	0.006	28.00	0.9877	0.9774	0.983	0.983	0.005	28.50	0.9891	0.9799	0.985	0.985	0.005
29.00	0.9904	0.9821	0.986	0.986	0.004	29.50	0.9915	0.9840	0.988	0.988	0.004	30.00	0.9925	0.9858	0.989	0.989	0.003
30.50	0.9934	0.9874	0.990	0.990	0.003	31.00	0.9942	0.9888	0.991	0.991	0.003	31.50	0.9948	0.9900	0.992	0.992	0.002
32.00	0.9955	0.9912	0.993	0.993	0.002	32.50	0.9960	0.9922	0.994	0.994	0.002	33.00	0.9965	0.9931	0.995	0.995	0.002
33.50	0.9969	0.9939	0.995	0.995	0.002	34.00	0.9973	0.9946	0.996	0.996	0.001	34.50	0.9976	0.9952	0.996	0.996	0.001
35.00	0.9979	0.9958	0.997	0.997	0.001	35.50	0.9982	0.9963	0.997	0.997	0.001	36.00	0.9984	0.9967	0.998	0.998	0.001
36.50	0.9986	0.9971	0.998	0.998	0.001	37.00	0.9988	0.9975	0.998	0.998	0.001	37.50	0.9990	0.9978	0.998	0.998	0.001
38.00	0.9991	0.9981	0.999	0.999	0.001	38.50	0.9992	0.9983	0.999	0.999	0.000	39.00	0.9993	0.9985	0.999	0.999	0.000
39.50	0.9994	0.9987	0.999	0.999	0.000	40.00	0.9995	0.9989	0.999	0.999	0.000	40.50	0.9996	0.9990	0.999	0.999	0.000
41.00	0.9996	0.9991	0.999	0.999	0.000	41.50	0.9997	0.9993	0.999	0.999	0.000	42.00	0.9997	0.9994	1.000	1.000	0.000
42.50	0.9998	0.9994	1.000	1.000	0.000	43.00	0.9998	0.9995	1.000	1.000	0.000	43.50	0.9999	0.9996	1.000	1.000	0.000
44.00	0.9999	0.9997	1.000	1.000	0.000	44.50	0.9999	0.9997	1.000	1.000	0.000	45.00	0.9999	0.9998	1.000	1.000	0.000
45.50	0.9999	0.9998	1.000	1.000	0.000	46.00	1.0000	0.9998	1.000	1.000	0.000	46.50	1.0000	0.9999	1.000	1.000	0.000
47.00	1.0000	0.9999	1.000	1.000	0.000	47.50	1.0000	1.0000	1.000	1.000	0.0						

AREA 9.9993

NUMBER OF TRANSFER UNITS = 40.000

T	X	Y	XSTAR	YSTAR	RATE	T	X	Y	XSTAR	YSTAR	RATE	T	X	Y	XSTAR	YSTAR	RATE
7.00	0.0001	0.0000	0.000	0.000	0.000	8.00	0.0003	0.0001	0.000	0.000	0.000	9.00	0.0006	0.0002	0.000	0.000	0.000
10.00	0.0011	0.0005	0.001	0.001	0.000	11.00	0.0018	0.0009	0.001	0.001	0.000	12.00	0.0028	0.0014	0.002	0.002	0.001
13.00	0.0043	0.0023	0.003	0.003	0.001	14.00	0.0064	0.0035	0.005	0.005	0.001	15.00	0.0092	0.0053	0.007	0.007	0.002
16.00	0.0129	0.0076	0.010	0.010	0.003	17.00	0.0175	0.0106	0.014	0.014	0.003	18.00	0.0234	0.0146	0.019	0.019	0.004
19.00	0.0305	0.0196	0.025	0.025	0.005	20.00	0.0392	0.0257	0.032	0.032	0.007	21.00	0.0494	0.0332	0.041	0.041	0.008
22.00	0.0614	0.0421	0.052	0.052	0.010	23.00	0.0751	0.0526	0.064	0.064	0.011	24.00	0.0907	0.0647	0.078	0.078	0.013
25.00	0.1082	0.0787	0.093	0.093	0.015	26.00	0.1277	0.0944	0.111	0.111	0.017	27.00	0.1489	0.1120	0.130	0.130	0.018
28.00	0.1720	0.1314	0.152	0.152	0.020	29.00	0.1968	0.1527	0.175	0.175	0.022	30.00	0.2231	0.1756	0.199	0.199	0.024
31.00	0.2508	0.2002	0.226	0.226	0.025	32.00	0.2798	0.2263	0.253	0.253	0.027	33.00	0.3099	0.2537	0.282	0.282	0.028
34.00	0.3407	0.2824	0.312	0.312	0.029	35.00	0.3723	0.3121	0.342	0.342	0.030	36.00	0.4042	0.3426	0.373	0.373	0.031
37.00	0.4363	0.3737	0.405	0.405	0.031	38.00	0.4684	0.4052	0.437	0.437	0.032	39.00	0.5003	0.4369	0.469	0.469	0.032
40.00	0.5318	0.4686	0.500	0.500	0.032	41.00	0.5628	0.5001	0.531	0.531	0.031	42.00	0.5929	0.5312	0.562	0.562	0.031
43.00	0.6222	0.5617	0.592	0.592	0.030	44.00	0.6505	0.5915	0.621	0.621	0.029	45.00	0.6776	0.6205	0.649	0.649	0.029
46.00	0.7036	0.6485	0.676	0.676	0.028	47.00	0.7283	0.6755	0.702	0.702	0.026	48.00	0.7516	0.7012	0.726	0.726	0.025
49.00	0.7737	0.7258	0.750	0.750	0.024	50.00	0.7943	0.7490	0.772	0.772	0.023	51.00	0.8137	0.7710	0.792	0.792	0.021
52.00	0.8316	0.7916	0.812	0.812	0.020	53.00	0.8483	0.8109	0.830	0.830	0.019	54.00	0.8637	0.8289	0.846	0.846	0.017
55.00	0.8779	0.8456	0.862	0.862	0.016	56.00	0.8909	0.8611	0.876	0.876	0.015	57.00	0.9027	0.8754	0.889	0.889	0.014
58.00	0.9135	0.8884	0.901	0.901	0.013	59.00	0.9233	0.9004	0.912	0.912	0.011	60.00	0.9322	0.9113	0.922	0.922	0.010
61.00	0.9402	0.9212	0.931	0.931	0.009	62.00	0.9473	0.9302	0.939	0.939	0.009	63.00	0.9537	0.9383	0.946	0.946	0.008
64.00	0.9595	0.9456	0.953	0.953	0.007	65.00	0.9646	0.9522	0.958	0.958	0.006	66.00	0.9691	0.9580	0.964	0.964	0.006
67.00	0.9731	0.9632	0.968	0.968	0.005	68.00	0.9767	0.9679	0.972	0.972	0.004	69.00	0.9798	0.9720	0.976	0.976	0.004
70.00	0.9825	0.9757	0.979	0.979	0.003	71.00	0.9849	0.9789	0.982	0.982	0.003	72.00	0.9870	0.9817	0.984	0.984	0.003
73.00	0.9889	0.9842	0.987	0.987	0.002	74.00	0.9905	0.9864	0.988	0.988	0.002	75.00	0.9919	0.9883	0.990	0.990	0.002
76.00	0.9930	0.9899	0.991	0.991	0.002	77.00	0.9941	0.9914	0.993	0.993	0.001	78.00	0.9950	0.9926	0.994	0.994	0.001
79.00	0.9957	0.9937	0.995	0.995	0.001	80.00	0.9964	0.9947	0.996	0.996	0.001	81.00	0.9970	0.9955	0.996	0.996	0.001
82.00	0.9975	0.9962	0.997	0.997	0.001	83.00	0.9979	0.9968	0.997	0.997	0.001	84.00	0.9982	0.9973	0.998	0.998	0.000
85.00	0.9985	0.9977	0.998	0.998	0.000	86.00	0.9988	0.9981	0.998	0.998	0.000	87.00	0.9990	0.9984	0.999	0.999	0.000
88.00	0.9992	0.9987	0.999	0.999	0.000	89.00	0.9993	0.9989	0.999	0.999	0.000	90.00	0.9995	0.9991	0.999	0.999	0.000
91.00	0.9996	0.9993	0.999	0.999	0.000	92.00	0.9997	0.9994	1.000	1.000	0.000	93.00	0.9998	0.9995	1.000	1.000	0.000
94.00	0.9998	0.9996	1.000	1.000	0.000	95.00	0.9999	0.9997	1.000	1.000	0.000	96.00	0.9999	0.9998	1.000	1.000	0.000
97.00	1.0000	0.9999	1.000	1.000	0.000	98.00	1.0000	1.0000	1.000	1.000	0.0						

AREA 39.999

APPENDIX 5C

PROGRAM LISTING - RATE (ASSEMBLER)

```
C
C
C     TEST OF RATE FUNCTION FOR IXLR PROGRAM
C
C
C     PURPOSE- TO EVALUATE RATE FOR COMBINATIONS OF
C
C          X          Y                    ZETA       K
C
C         0.0        0.0                   0.0        0.1
C         0.5        0.5                   0.1        0.5
C         1.0        1.0                   0.5        1.0
C                                          1.0        2.0
C                                          2.0       10.0
C                                         10.0
C                                       INFINITE
C
0001        LOGICAL LINEAR,LIMIT
0002        REAL K
0003        COMMON ZETA,K,RZETA,RZETAP,FAC1,FAC2,SIGMA,LINEAR,LIMIT,XSTAR,YSTA
           1R
0004        REAL Z(10)/0.0,0.1,0.5,1.0,2.0,10.0,-10.0,0.0,0.0,0.0/
C
C     LOOP FOR ALL ZETA
C
0005        DO 200 I=1,7
0006        WRITE(6,100)
0007      100 FORMAT('1 ZETA  K'4X'X'3X'Y'T24'R'T31'XSTAR'T40'YSTAR'T50'R1'T59'R
           12'T68'E1'T79'E2'/)
0008        ZETA=Z(I)
0009        RO=0.0
0010        SIGMA=1.0
0011        IF(ZETA.GT.1.0002)SIGMA=ZETA
0012        IF(ZETA.EQ.0.0) GO TO 2
0013        RZETA=1.0/ZETA
0014        RO=SIGMA/ZETA
0015      2 RZETAP=1.0/(ZETA+1.0)
0016        LIMIT=.FALSE.
0017        IF(ZETA.LT.0.0001) LIMIT=.TRUE.
C
C     INNER LOOP FOR ALL K
C
0018        DO 200 J=1,5
0019        WRITE(6,102)
0020      102 FORMAT(1H )
0021        K=Z(J+1)
0022        IF(K.LT.0.999.OR.K.GT.1.001) GO TO 7
C
C     FOR LINEAR EQUILIBRIUM
```

```
      C
0023        FAC1=1.0
0024        FAC2=1.0
0025        LINEAR=.TRUE.
0026        GO TO 8
      C
      C     NON-LINEAR EQUILIBRIUM
      C
0027      7 IF(ZETA.EQ.0.0)GOTO10
0028        FAC2=ZETA*(K-1.0)
0029        FAC1=(1.0+K*ZETA)/FAC2
0030        FAC2=K/FAC2
0031        GOTO11
0032     10 FAC1=1.0
0033        FAC2=1.0
0034     11 LINEAR=.FALSE.
      C
      C     INNER-MOST LOOPS FOR X AND Y
      C
0035      8 DO 200 K1=2,4
0036        DO 200 K2=2,4
0037        X=Z(K1)
0038        Y=Z(K2)
0039        R=RATE(X,Y)
0040        A=RO*(X-XSTAR)
0041        B=SIGMA*(YSTAR-Y)
0042        E1=YSTAR*(1.0-XSTAR)
0043        E2=K*XSTAR*(1.0-YSTAR)
0044        WRITE(6,101)ZETA,K,X,Y,R,XSTAR,YSTAR,A,B,E1,E2
0045    101 FORMAT(1H ,2F5.1,2F4.1,7F9.5)
0046    200 CONTINUE
0047        STOP
0048        END
```

```
FLGS  L.CTR    OBJCODE    ADDR    STMT      SOURCE STATEMENT

      000000                        1  SPRATE   START
                                    2  *
                                    3  * THIS SUBPROGRAM CALCULATES THE FUNCTION RATE(XX1,YY1) FOR THE IXLR
                                    4  *  PROGRAM
                                    5  * SET &W EQUAL TO 1 FOR DIAGNOSTIC REGISTER DUMPS
                              00000 6  &W       SETA  0                                    1  ATES       W&
                                    7          ENTRY RATE
      000000  D9C1E3C540            8          DC    CL5'RATE'
      000005  06                    9          DC    X'6'
                                   10          EXTRN SQRT
                                   11           AIF   (&W EQ 0).N1
                                   12  .N1      ANOP
                              00006 13          USING *,15
                                   14  *
                                   15  * STORE ALL REGISTERS
      000006  50ED 000C  0000C     16  RATE     ST    14,12(13)
      00000A  50FD 0010  00010     17          ST    15,16(13)
      00000E  500D 0014  00014     18          ST    0,20(13)
      000012  50CD 0044  00044     19          ST    12,68(13)
      000016  503D 0020  00020     20          ST    3,32(13)
      00001A  504D 0024  00024     21          ST    4,36(13)
      00001E  505D 0028  00028     22          ST    5,40(13)
      000022  50D0 F1FA  00200     23          ST    13,SAVE1
      000026  501D 0018  00018     24          ST    1,24(13)
      00002A  502D 001C  0001C     25          ST    2,28(13)
                                   26  *
                                   27  * REGISTER 12 IS TO BE THE BASE REGISTER
      00002E  18CF                 28          LR    12,15
                              00006 29          USING RATE,12
                                   30          DROP  15
                                   31  *
      000030  5840 C27A  00280     32          L     4,=X'00006200'
                                   33  * REGISTER 4 CONTAINS THE ADDRESS OF THE COMMON AREA WHICH CONTAINS
                                   34  * ZETA,K,RZETA,RZETAP,FAC1,FAC2,LAMDA,LINEAR,LIMIT,XSTAR,YSTAR
                                   35  *
                                   36  * LIMIT IS TRUE FOR PARTICLE OR FILM CONTROL
                                   37  * REGISTER 1 CONTAINS THE ADDRESS OF THE ARGUMENT LIST XX1,YY1
                                   38  *
                                   39  * CALCULATE ALFA AND STORE XX1 AND YY1
      000034  5831 0000  00000     40          L     3,0(1)    REG3=ADDRESS XX1
      000038  5821 0004  00004     41          L     2,4(1)    REG2=ADDRESS YY1
      00003C  7822 0000  00000     42          LE    2,0(2)    FPREG=YY1
      000040  7020 C272  00278     43          STE   2,YY1
                                   44           AIF   (&W EQ 0).N2
                                   45  .N2      ANOP
      000044  7C24 0000  00000     46          ME    2,0(4)              *ZETA
      000048  7A23 0000  00000     47          AE    2,0(3)                   +XX1=ALFA
      00004C  7843 0000  00000     48          LE    4,0(3)
      000050  7040 C26E  00274     49          STE   4,XX1
                                   50  *
                                   51  * TEST FOR LINEAR EQUILIBRIUM
      000054  5834 001C  0001C     52          L     3,28(4)   REG3= LINEAR
      000058  5930 C28E  00294     53          C     3,=F'1'
      00005C  4770 C0A0  000A6     54          BNE   NONLIN
                                   55  *
```

```
FLGS   L.CTR     OBJCODE    ADDR    STMT      SOURCE STATEMENT

                                      56  * THIS SECTION PROVIDES FOR LINEAR EQUILIBRIUM
                                      57  *
                                      58  * TEST FOR LIMITING ZETA
                                      59  *
       000060  5834 0020   00020     60           L     3,32(4)   GPR3=LIMIT
       000064  5930 C28E   00294     61           C     3,=F'1'
       000068  4780 C074   0007A     62           BE    LIMZL     BRANCH IF LIMIT TRUE
                                      63  *
                                      64  * ZETA IN INTERMEDIATE RANGE,MIXED CONTROL,LINEAR EQUILIBRIUM
                                      65  *
       00006C  7844 000C   0000C     66           LE    4,12(4)   FPREG4=RZETAP
       000070  3C42                 67           MER   4,2                     *ALFA=YSTAR
       000072  7040 C26A   00270     68           STE   4,YSTAR
       000076  47F0 C132   00138     69           B     CALCRATE
                                      70  *
                                      71  * PARTICLE OR FILM CONTROL,LINEAR
                                      72  *
       00007A  7824 0000   00000     73  LIMZL    LE    2,0(4)    FPR2=ZETA
       00007E  7920 C282   00288     74           CE    2,=E'-1.0'
       000082  4720 C088   0008E     75           BH    ZETAZERL  BRANCH IF ZETA ZERO
       000086  7820 C272   00278     76           LE    2,YY1     ZETA=INFINITY,FILM CONTROL
       00008A  47F0 C08C   00092     77           B     *+8       FPR2=YY1
       00008E  7820 C26E   00274     78  ZETAZERL LE    2,XX1     FPR2=XX1,ZETA=ZERO,PARTICLE CONTROL
       000092  7020 C266   0026C     79           STE   2,XSTAR
       000096  7020 C26A   00270     80           STE   2,YSTAR
       00009A  7800 C26E   00274     81           LE    0,XX1     FPR0=XX1
       00009E  7B00 C272   00278     82           SE    0,YY1             -YY1=RATE
       0000A2  47F0 C1B8   001BE     83           B     BACK
                                      84  *
                                      85  * FOR NONLINEAR EQUILIBRIUM
                                      86  *
                                      87  * TEST FOR LIMITING ZETA
                                      88  *
       0000A6  5834 0020   00020     89  NONLIN   L     3,32(4)
       0000AA  5930 C28E   00294     90           C     3,=F'1'
       0000AE  4780 C162   00168     91           BE    LIMZ      BRANCH IF LIMIT TRUE
                                      92  *
                                      93  * MIXED CONTROL,NONLINEAR EQUILIBRIUM
                                      94  *
                                      95  * CALCULATE B
                                      96  *
       0000B2  3842                  97           LER   4,2       FPREG4=ALFA
       0000B4  7C44 0008   00008     98           ME    4,8(4)              *RZETA
       0000B8  7A44 0010   00010     99           AE    4,16(4)                     +FAC1=-B
       0000BC  3344                 100           LCER  4,4       FPREG4=B
                                     101  *
                                     102  * CALCULATE C
       0000BE  7C24 0014   00014    103           ME    2,20(4)   FPREG2=ALFA*FAC2
       0000C2  7020 C252   00258    104           STE   2,C
                                     105  *
                                     106  * CALCULATE PAR
       0000C6  3864                 107           LER   6,4       FPREG6=B
       0000C8  7C60 C292   00298    108           ME    6,=E'-.5'       *-.5=PAR
       0000CC  7060 C1FE   00204    109           STE   6,PAR
                                     110  *
```

```
FLGS  L.CTR     OBJCODE   ADDR    STMT     SOURCE STATEMENT
                                   111  * CALCULATE DISCRIMINANT B*B-4C
      0000D0    7C20 C286 0028C   112           ME    2,=E'+4.0'      FPREG2=+4*C
      0000D4    3C44              113           MER   4,4        FPREG4=B*B
      0000D6    3B42              114           SER   4,2                -4*C
      0000D8    7040 C202 00208   115           STE   4,DISCRIM
                                   116  *
                                   117  *
                                   118  * CALL SQRT,PLACED IN FPREGO
      0000DC    92FF C1F6 001FC   119           MVI   PARAM,X'FF'             END OF ARGUMENT LIST FLAG
      0000E0    4110 C1F6 001FC   120           LA    1,PARAM
      0000E4    41D0 C206 0020C   121           LA    13,SAVE
      0000E8    58F0 C28A 00290   122           L     15,=A(SQRT)
      0000EC    05EF              123           BALR  14,15
      0000EE    7C00 C296 0029C   124           ME    0,=E'0.5'
      0000F2    7000 C24E 00254   125           STE   0,DIS           FPREGO=DIS
                                   126  *
                                   127  * FORM ROOTS
      0000F6    7820 C1FE 00204   128           LE    2,PAR           FPREG2=PAR
      0000FA    3222              129           LTER  2,2
      0000FC    4720 C100 00106   130           BC    2,PARPOS        BRANCH IF PAR POSITIVE
      000100    3B20              131  PARNEG   SER   2,0             FPREG2=PAR-DIS
      000102    47F0 C102 00108   132           B     OTHER
      000106    3A20              133  PARPOS   AER   2,0             FPREG2=PAR+DIS
      000108    7020 C256 0025C   134  OTHER    STE   2,ROOT1
      00010C    7840 C252 00258   135           LE    4,C             FPREG4=C
      000110    3D42              136           DER   4,2                     /ROOT1=ROOT2
      000112    7040 C25A 00260   137           STE   4,ROOT2
                                   138  *
                                   139  * SELECT CORRECT ROOT,THAT NEARER 0.5
                                   140  *
      000116    7B20 C296 0029C   141           SE    2,=E'0.5'       FPR2=E1=ROOT1-0.5
      00011A    7B40 C296 0029C   142           SE    4,=E'0.5'       FPR2=E2=ROOT2-0.5
                                   143  *
      00011E    3022              144           LPER  2,2             TAKE ABSOLUTE VALUES
      000120    3044              145           LPER  4,4
      000122    3B24              146           SER   2,4             FPR2=E1-E2
      000124    4720 C12A 00130   147           BP    USERT2          BRANCH TO USE ROOT2 IF E1.GT.E2
      000128    7840 C256 0025C   148  USERT1   LE    4,ROOT1         OTHERWISE USE ROOT1
      00012C    47F0 C12E 00134   149           B     *+8
      000130    7840 C25A 00260   150  USERT2   LE    4,ROOT2
      000134    7040 C26A 00270   151           STE   4,YSTAR
                                   152  *
                                   153  *        CALCULATE XSTAR AND RATE
      000138    3824              154  CALCRATE LER   2,4       FPR2=YSTAR
      00013A    7800 C27E 00284   155           LE    0,=E'1.0' FPRO=1.0
      00013E    3B02              156           SER   0,2                -YSTAR)
      000140    7C04 0004 00004   157           ME    0,4(4)                  *K
      000144    3A02              158           AER   0,2       FPRO=YSTAR+K(1-YSTAR)
      000146    3D20              159           DER   2,0       FPR2=XSTAR
      000148    7020 C266 0026C   160           STE   2,XSTAR
                                   161  *
      00014C    7800 C26A 00270   162           LE    0,YSTAR
      000150    58D0 C1FA 00200   163           L     13,SAVE1
      000154    581D 0018 00018   164           L     1,24(13)
      000158    5821 0004 00004   165           L     2,4(1)
```

```
FLGS   L.CTR    OBJCODE   ADDR   STMT      SOURCE STATEMENT

       00015C   7B02 0000 00000   166           SE    0,0(2)
       000160   7C04 0018 00018   167           ME    0,24(4)
                                  168  *
       000164   47F0 C1B8 001BE   169           B     BACK
                                  170  * PARTICLE OR FILM CONTROL,NONLINEAR
                                  171  *
                                  172  *
                                  173  *
       000168   7824 0000 00000   174  LIMZ     LE    2,0(4)     FPR2=ZETA
       00016C   7920 C282 00288   175           CE    2,=E'-1.0'
       000170   4720 C194 0019A   176           BH    ZETAZERO   BRANCH IF ZETA ZERO
                                  177  *
                                  178  * FOR ZETA INFINITE,IE FILM CONTROL
                                  179  *
       000174   7820 C272 00278   180           LE    2,YY1      FPR2=YY1
       000178   7020 C26A 00270   181           STE   2,YSTAR    YSTAR=YY1
                                  182  *
                                  183  *        CALCULATE XSTAR
       00017C   7800 C27E 00284   184           LE    0,=E'1.0' FPR0=1.0
       000180   3B02              185           SER   0,2                -YY1)
       000182   7C04 0004 00004   186           ME    0,4(4)                *K
       000186   3A02              187           AER   0,2        FPR0=YY1+K(1-YY1)
       000188   3D20              188           DER   2,0        FPR2=XSTAR
       00018A   7020 C266 0026C   189           STE   2,XSTAR
       00018E   7820 C26E 00274   190           SE    2,XX1      FPR2=XSTAR-XX1
       000192   3B00              191           SER   0,0
       000194   3B02              192           SER   0,2        FPR0=RATE
       000196   47F0 C1B8 001BE   193           B     BACK
                                  194  *
                                  195  * FOR ZETA ZERO,IE PARTICLE CONTROL
                                  196  *
       00019A   7820 C26E 00274   197  ZETAZERO LE    2,XX1      FPR2=XX1
       00019E   7020 C266 0026C   198           STE   2,XSTAR    XSTAR=XX1
       0001A2   7800 C27E 00284   199           LE    0,=E'1.0' FPR0=1.0
       0001A6   3B02              200           SER   0,2                -XX1
       0001A8   7C24 0004 00004   201           ME    2,4(4)     FPR2=K*XX1
       0001AC   3A02              202           AER   0,2        FPR0=1+(K-1)*XX1
       0001AE   3D20              203           DER   2,0        FPR2= YSTAR
       0001B0   7020 C26A 00270   204           STE   2,YSTAR
       0001B4   7820 C272 00278   205           SE    2,YY1      FPR2=YSTAR-YY1=RATE
       0001B8   3B02              206           LER   0,2        FPR0=RATE
       0001BA   47F0 C1B8 001BE   207           B     BACK
                                  208  *
                                  209  * REPLACE XSTAR,YSTAR IN COMMON
                                  210  *
       0001BE   7820 C266 0026C   211  BACK     LE    2,XSTAR
       0001C2   7024 0024 00024   212           STE   2,36(4)
       0001C6   7820 C26A 00270   213           LE    2,YSTAR
       0001CA   7024 0028 00028   214           STE   2,40(4)
                                  215  * RESTORE REGISTERS
       0001CE   58D0 C1FA 00200   216           L     13,SAVE1
       0001D2   581D 0018 00018   217           L     1,24(13)
       0001D6   582D 001C 0001C   218           L     2,28(13)
       0001DA   583D 0020 00020   219           L     3,32(13)
       0001DE   584D 0024 00024   220           L     4,36(13)
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FLGS   L.CTR     OBJCODE    ADDR    STMT      SOURCE STATEMENT

       0001E2  585D 0028  00028    221              L      5,40(13)
       0001E6  58ED 000C  0000C    222              L      14,12(13)
       0001EA  58FD 0010  00010    223              L      15,16(13)
       0001EE  580D 0014  00014    224              L      0,20(13)
                                   225  *
                                   226  * RETURN TO MAINLINE
                                   227  *
       0001F2  92FF D00C  0000C    228              MVI    12(13),X'FF'
       0001F6  58CD 0044  00044    229              L      12,68(13)
       0001FA  07FE                230              BCR    15,14
                                   231               AIF   (&W EQ 0).N5
                                   232  .N5         ANOP
                                   233  * SYMBOL TABLE AREA
       0001FC                      234              DS     0F
       0001FC  00000208            235  PARAM       DC     A(DISCRIM)
       000200                      236  SAVE1       DS     F
       000204                      237  PAR         DS     E
       000208                      238  DISCRIM     DS     E
       00020C                      239  SAVE        DS     18F
       000254                      240  DIS         DS     E
       000258                      241  C           DS     E
       00025C                      242  ROOT1       DS     E
       000260                      243  ROOT2       DS     E
       000264  00000000            244  ZERO        DC     E'0.0'
       000268  41100000            245  ONE         DC     E'1.0'
       00026C                      246  XSTAR       DS     E
       000270                      247  YSTAR       DS     E
       000274                      248  XX1         DS     E
       000278                      249  YY1         DS     E
                                +  250   LTORG
       000280  00006200         +  251   DC   X'00006200'
       000284  41100000         +  252   DC   E'1.0'
       000288  C1100000         +  253   DC   E'-1.0'
       00028C  41400000         +  254   DC   E'+4.0'
       000290  00000000         +  255   DC   A(SQRT)
       000294  00000001         +  256   DC   F'1'
       000298  C0800000         +  257   DC   E'-.5'
       00029C  40800000         +  258   DC   E'0.5'
                                   259              END
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ZETA	K	X	Y	R	XSTAR	YSTAR	R1	R2	E1	E2
0.0	0.1	0.1	0.1	-0.08901	0.10000	0.01099	0.0	-0.08901	0.00989	0.00989
0.0	0.1	0.1	0.5	-0.48901	0.10000	0.01099	0.0	-0.48901	0.00989	0.00989
0.0	0.1	0.1	1.0	-0.98901	0.10000	0.01099	0.0	-0.98901	0.00989	0.00989
0.0	0.1	0.5	0.1	-0.00909	0.50000	0.09091	0.0	-0.00909	0.04545	0.04545
0.0	0.1	0.5	0.5	-0.40909	0.50000	0.09091	0.0	-0.40909	0.04545	0.04545
0.0	0.1	0.5	1.0	-0.90909	0.50000	0.09091	0.0	-0.90909	0.04545	0.04545
0.0	0.1	1.0	0.1	0.90000	1.00000	1.00000	0.0	0.90000	0.0	0.0
0.0	0.1	1.0	0.5	0.50000	1.00000	1.00000	0.0	0.50000	0.0	0.0
0.0	0.1	1.0	1.0	0.0	1.00000	1.00000	0.0	0.0	0.0	0.0
0.0	0.5	0.1	0.1	-0.04737	0.10000	0.05263	0.0	-0.04737	0.04737	0.04737
0.0	0.5	0.1	0.5	-0.44737	0.10000	0.05263	0.0	-0.44737	0.04737	0.04737
0.0	0.5	0.1	1.0	-0.94737	0.10000	0.05263	0.0	-0.94737	0.04737	0.04737
0.0	0.5	0.5	0.1	0.23333	0.50000	0.33333	0.0	0.23333	0.16667	0.16667
0.0	0.5	0.5	0.5	-0.16667	0.50000	0.33333	0.0	-0.16667	0.16667	0.16667
0.0	0.5	0.5	1.0	-0.66667	0.50000	0.33333	0.0	-0.66667	0.16667	0.16667
0.0	0.5	1.0	0.1	0.90000	1.00000	1.00000	0.0	0.90000	0.0	0.0
0.0	0.5	1.0	0.5	0.50000	1.00000	1.00000	0.0	0.50000	0.0	0.0
0.0	0.5	1.0	1.0	0.0	1.00000	1.00000	0.0	0.0	0.0	0.0
0.0	1.0	0.1	0.1	0.0	0.10000	0.10000	0.0	0.0	0.09000	0.09000
0.0	1.0	0.1	0.5	-0.40000	0.10000	0.10000	0.0	-0.40000	0.09000	0.09000
0.0	1.0	0.1	1.0	-0.90000	0.10000	0.10000	0.0	-0.90000	0.09000	0.09000
0.0	1.0	0.5	0.1	0.40000	0.50000	0.50000	0.0	0.40000	0.25000	0.25000
0.0	1.0	0.5	0.5	0.0	0.50000	0.50000	0.0	0.0	0.25000	0.25000
0.0	1.0	0.5	1.0	-0.50000	0.50000	0.50000	0.0	-0.50000	0.25000	0.25000
0.0	1.0	1.0	0.1	0.90000	1.00000	1.00000	0.0	0.90000	0.0	0.0
0.0	1.0	1.0	0.5	0.50000	1.00000	1.00000	0.0	0.50000	0.0	0.0
0.0	1.0	1.0	1.0	0.0	1.00000	1.00000	0.0	0.0	0.0	0.0
0.0	2.0	0.1	0.1	0.08182	0.10000	0.18182	0.0	0.08182	0.16364	0.16364
0.0	2.0	0.1	0.5	-0.31818	0.10000	0.18182	0.0	-0.31818	0.16364	0.16364
0.0	2.0	0.1	1.0	-0.81818	0.10000	0.18182	0.0	-0.81818	0.16364	0.16364
0.0	2.0	0.5	0.1	0.56667	0.50000	0.66667	0.0	0.56667	0.33333	0.33333
0.0	2.0	0.5	0.5	0.16667	0.50000	0.66667	0.0	0.16667	0.33333	0.33333
0.0	2.0	0.5	1.0	-0.33333	0.50000	0.66667	0.0	-0.33333	0.33333	0.33333
0.0	2.0	1.0	0.1	0.90000	1.00000	1.00000	0.0	0.90000	0.0	0.0
0.0	2.0	1.0	0.5	0.50000	1.00000	1.00000	0.0	0.50000	0.0	0.0
0.0	2.0	1.0	1.0	0.0	1.00000	1.00000	0.0	0.0	0.0	0.0
0.0	10.0	0.1	0.1	0.42632	0.10000	0.52632	0.0	0.42632	0.47368	0.47368
0.0	10.0	0.1	0.5	0.02632	0.10000	0.52632	0.0	0.02632	0.47368	0.47368
0.0	10.0	0.1	1.0	-0.47368	0.10000	0.52632	0.0	-0.47368	0.47368	0.47368
0.0	10.0	0.5	0.1	0.80909	0.50000	0.90909	0.0	0.80909	0.45455	0.45455
0.0	10.0	0.5	0.5	0.40909	0.50000	0.90909	0.0	0.40909	0.45455	0.45455
0.0	10.0	0.5	1.0	-0.09091	0.50000	0.90909	0.0	-0.09091	0.45455	0.45455
0.0	10.0	1.0	0.1	0.90000	1.00000	1.00000	0.0	0.90000	0.0	0.0
0.0	10.0	1.0	0.5	0.50000	1.00000	1.00000	0.0	0.50000	0.0	0.0
0.0	10.0	1.0	1.0	0.0	1.00000	1.00000	0.0	0.0	0.0	0.0

ZETA	K	X	Y	R	XSTAR	YSTAR	R1	R2	E1	E2
0.5	0.1	0.1	0.1	-0.08374	0.14187	0.01626	-0.08374	-0.08374	0.01396	0.01396
0.5	0.1	0.1	0.5	-0.45369	0.32685	0.04631	-0.45369	-0.45369	0.03117	0.03117
0.5	0.1	0.1	1.0	-0.89254	0.54627	0.10746	-0.89254	-0.89254	0.04876	0.04876
0.5	0.1	0.5	0.1	-0.00779	0.50390	0.09221	-0.00780	-0.00779	0.04574	0.04574
0.5	0.1	0.5	0.5	-0.33333	0.66667	0.16667	-0.33333	-0.33333	0.05556	0.05556
0.5	0.1	0.5	1.0	-0.66667	0.83333	0.33333	-0.66667	-0.66667	0.05556	0.05556
0.5	0.1	1.0	0.1	0.28027	0.85987	0.38027	0.28027	0.28027	0.05329	0.05329
0.5	0.1	1.0	0.5	0.11693	0.94154	0.61693	0.11693	0.11693	0.03607	0.03607
0.5	0.1	1.0	1.0	0.00000	1.00000	1.00000	-0.00000	0.00000	-0.00000	-0.00000
0.5	0.5	0.1	0.1	-0.03701	0.11851	0.06299	-0.03701	-0.03701	0.05552	0.05552
0.5	0.5	0.1	0.5	-0.34295	0.27147	0.15705	-0.34295	-0.34295	0.11442	0.11442
0.5	0.5	0.1	1.0	-0.70683	0.45341	0.29317	-0.70683	-0.70683	0.16024	0.16024
0.5	0.5	0.5	0.1	0.16416	0.41792	0.26416	0.16416	0.16416	0.15376	0.15376
0.5	0.5	0.5	0.5	-0.11400	0.55700	0.38600	-0.11400	-0.11400	0.17100	0.17100
0.5	0.5	0.5	1.0	-0.43845	0.71922	0.56155	-0.43845	-0.43845	0.15767	0.15767
0.5	0.5	1.0	0.1	0.50000	0.75000	0.60000	0.50000	0.50000	0.15000	0.15000
0.5	0.5	1.0	0.5	0.26556	0.86722	0.76556	0.26556	0.26556	0.10165	0.10165
0.5	0.5	1.0	1.0	0.0	1.00000	1.00000	0.0	0.0	0.0	0.0
0.5	1.0	0.1	0.1	-0.00000	0.10000	0.10000	0.00000	-0.00000	0.09000	0.09000
0.5	1.0	0.1	0.5	-0.26667	0.23333	0.23333	-0.26667	-0.26667	0.17889	0.17889
0.5	1.0	0.1	1.0	-0.60000	0.40000	0.40000	-0.60000	-0.60000	0.24000	0.24000
0.5	1.0	0.5	0.1	0.26667	0.36667	0.36667	0.26667	0.26667	0.23222	0.23222
0.5	1.0	0.5	0.5	-0.00000	0.50000	0.50000	0.00000	-0.00000	0.25000	0.25000
0.5	1.0	0.5	1.0	-0.33333	0.66667	0.66667	-0.33333	-0.33333	0.22222	0.22222
0.5	1.0	1.0	0.1	0.60000	0.70000	0.70000	0.60000	0.60000	0.21000	0.21000
0.5	1.0	1.0	0.5	0.33333	0.83333	0.83333	0.33333	0.33333	0.13889	0.13889
0.5	1.0	1.0	1.0	-0.00000	1.00000	1.00000	0.00000	-0.00000	0.00000	0.00000
0.5	2.0	0.1	0.1	0.04438	0.07781	0.14438	0.04438	0.04438	0.13315	0.13315
0.5	2.0	0.1	0.5	-0.18039	0.19020	0.31961	-0.18039	-0.18039	0.25882	0.25882
0.5	2.0	0.1	1.0	-0.48806	0.34403	0.51194	-0.48806	-0.48806	0.33582	0.33582
0.5	2.0	0.5	0.1	0.37575	0.31212	0.47575	0.37575	0.37575	0.32726	0.32726
0.5	2.0	0.5	0.5	0.11400	0.44300	0.61400	0.11400	0.11400	0.34200	0.34200
0.5	2.0	0.5	1.0	-0.23607	0.61803	0.76393	-0.23607	-0.23607	0.29180	0.29180
0.5	2.0	1.0	0.1	0.69113	0.65444	0.79113	0.69113	0.69113	0.27339	0.27339
0.5	2.0	1.0	0.5	0.39150	0.80425	0.89150	0.39150	0.39150	0.17451	0.17451
0.5	2.0	1.0	1.0	0.0	1.00000	1.00000	0.0	0.0	0.0	0.0
0.5	10.0	0.1	0.1	0.13908	0.03046	0.23908	0.13908	0.13908	0.23179	0.23179
0.5	10.0	0.1	0.5	0.01087	0.09457	0.51087	0.01087	0.01087	0.46256	0.46256
0.5	10.0	0.1	1.0	-0.25402	0.22701	0.74598	-0.25402	-0.25402	0.57664	0.57664
0.5	10.0	0.5	0.1	0.60868	0.19566	0.70867	0.60868	0.60868	0.57001	0.57001
0.5	10.0	0.5	0.5	0.33333	0.33333	0.83333	0.33333	0.33333	0.55556	0.55556
0.5	10.0	0.5	1.0	-0.07869	0.53934	0.92131	-0.07869	-0.07869	0.42441	0.42441
0.5	10.0	1.0	0.1	0.83333	0.58333	0.93333	0.83334	0.83333	0.38889	0.38889
0.5	10.0	1.0	0.5	0.47018	0.76491	0.97018	0.47018	0.47018	0.22808	0.22808
0.5	10.0	1.0	1.0	0.0	1.00000	1.00000	0.0	0.0	0.0	0.0

ZETA	K	X	Y	R	XSTAR	YSTAR	R1	R2	E1	E2
1.0	0.1	0.1	0.1	-0.07870	0.17870	0.02130	-0.07870	-0.07870	0.01749	0.01749
1.0	0.1	0.1	0.5	-0.40681	0.50681	0.09319	-0.40681	-0.40681	0.04596	0.04596
1.0	0.1	0.1	1.0	-0.70621	0.80621	0.29379	-0.70621	-0.70621	0.05693	0.05693
1.0	0.1	0.5	0.1	-0.00681	0.50681	0.09319	-0.00681	-0.00681	0.04596	0.04596
1.0	0.1	0.5	0.5	-0.25975	0.75975	0.24025	-0.25975	-0.25975	0.05772	0.05772
1.0	0.1	0.5	1.0	-0.42988	0.92988	0.57012	-0.42988	-0.42988	0.03997	0.03997
1.0	0.1	1.0	0.1	0.19379	0.80621	0.29379	0.19379	0.19379	0.05693	0.05693
1.0	0.1	1.0	0.5	0.07012	0.92988	0.57012	0.07012	0.07012	0.03997	0.03997
1.0	0.1	1.0	1.0	0.0	1.00000	1.00000	0.0	0.0	0.0	0.0
1.0	0.5	0.1	0.1	-0.03031	0.13031	0.06969	-0.03031	-0.03031	0.06061	0.06061
1.0	0.5	0.1	0.5	-0.27171	0.37171	0.22829	-0.27171	-0.27171	0.14343	0.14343
1.0	0.5	0.1	1.0	-0.53490	0.63490	0.46510	-0.53490	-0.53490	0.16981	0.16981
1.0	0.5	0.5	0.1	0.12829	0.37171	0.22829	0.12829	0.12829	0.14343	0.14343
1.0	0.5	0.5	0.5	-0.08579	0.58579	0.41421	-0.08579	-0.08579	0.17157	0.17157
1.0	0.5	0.5	1.0	-0.31386	0.81386	0.68614	-0.31386	-0.31386	0.12772	0.12772
1.0	0.5	1.0	0.1	0.36510	0.63490	0.46510	0.36510	0.36510	0.16981	0.16981
1.0	0.5	1.0	0.5	0.18614	0.81386	0.68614	0.18614	0.18614	0.12772	0.12772
1.0	0.5	1.0	1.0	0.0	1.00000	1.00000	0.0	0.0	0.0	0.0
1.0	1.0	0.1	0.1	0.0	0.10000	0.10000	0.0	0.0	0.09000	0.09000
1.0	1.0	0.1	0.5	-0.20000	0.30000	0.30000	-0.20000	-0.20000	0.21000	0.21000
1.0	1.0	0.1	1.0	-0.45000	0.55000	0.55000	-0.45000	-0.45000	0.24750	0.24750
1.0	1.0	0.5	0.1	0.20000	0.30000	0.30000	0.20000	0.20000	0.21000	0.21000
1.0	1.0	0.5	0.5	0.0	0.50000	0.50000	0.0	0.0	0.25000	0.25000
1.0	1.0	0.5	1.0	-0.25000	0.75000	0.75000	-0.25000	-0.25000	0.18750	0.18750
1.0	1.0	1.0	0.1	0.45000	0.55000	0.55000	0.45000	0.45000	0.24750	0.24750
1.0	1.0	1.0	0.5	0.25000	0.75000	0.75000	0.25000	0.25000	0.18750	0.18750
1.0	1.0	1.0	1.0	0.0	1.00000	1.00000	0.0	0.0	0.0	0.0
1.0	2.0	0.1	0.1	0.03031	0.06969	0.13031	0.03031	0.03031	0.12122	0.12122
1.0	2.0	0.1	0.5	-0.12829	0.22829	0.37171	-0.12829	-0.12829	0.28686	0.28686
1.0	2.0	0.1	1.0	-0.36510	0.46510	0.63490	-0.36510	-0.36510	0.33961	0.33961
1.0	2.0	0.5	0.1	0.27171	0.22829	0.37171	0.27171	0.27171	0.28686	0.28686
1.0	2.0	0.5	0.5	0.08579	0.41421	0.58579	0.08579	0.08579	0.34315	0.34315
1.0	2.0	0.5	1.0	-0.18614	0.68614	0.81386	-0.18614	-0.18614	0.25544	0.25544
1.0	2.0	1.0	0.1	0.53490	0.46510	0.63490	0.53490	0.53490	0.33961	0.33961
1.0	2.0	1.0	0.5	0.31386	0.68614	0.81386	0.31386	0.31386	0.25544	0.25544
1.0	2.0	1.0	1.0	0.0	1.00000	1.00000	0.0	0.0	0.0	0.0
1.0	10.0	0.1	0.1	0.07870	0.02130	0.17870	0.07870	0.07870	0.17490	0.17490
1.0	10.0	0.1	0.5	0.00681	0.09319	0.50681	0.00681	0.00681	0.45959	0.45959
1.0	10.0	0.1	1.0	-0.19379	0.29379	0.80621	-0.19379	-0.19379	0.56935	0.56935
1.0	10.0	0.5	0.1	0.40681	0.09319	0.50681	0.40681	0.40681	0.45959	0.45959
1.0	10.0	0.5	0.5	0.25975	0.24025	0.75975	0.25975	0.25975	0.57722	0.57722
1.0	10.0	0.5	1.0	-0.07012	0.57012	0.92988	-0.07012	-0.07012	0.39974	0.39974
1.0	10.0	1.0	0.1	0.70621	0.29379	0.80621	0.70621	0.70621	0.56935	0.56935
1.0	10.0	1.0	0.5	0.42988	0.57012	0.92988	0.42988	0.42988	0.39974	0.39974
1.0	10.0	1.0	1.0	0.0	1.00000	1.00000	0.0	0.0	0.0	0.0

ZETA	K	X	Y	R	XSTAR	YSTAR	R1	R2	E1	E2
2.0	0.1	0.1	0.1	-0.13908	0.23908	0.03046	-0.13908	-0.13908	0.02318	0.02318
2.0	0.1	0.1	0.5	-0.60868	0.70867	0.19566	-0.60867	-0.60868	0.05700	0.05700
2.0	0.1	0.1	1.0	-0.83333	0.93333	0.58333	-0.83333	-0.83333	0.03889	0.03889
2.0	0.1	0.5	0.1	-0.01087	0.51087	0.09457	-0.01087	-0.01087	0.04626	0.04626
2.0	0.1	0.5	0.5	-0.33333	0.83333	0.33333	-0.33333	-0.33333	0.05556	0.05556
2.0	0.1	0.5	1.0	-0.47018	0.97018	0.76491	-0.47018	-0.47018	0.02281	0.02281
2.0	0.1	1.0	0.1	0.25402	0.74598	0.22701	0.25402	0.25402	0.05766	0.05766
2.0	0.1	1.0	0.5	0.07869	0.92131	0.53934	0.07869	0.07869	0.04244	0.04244
2.0	0.1	1.0	1.0	-0.00000	1.00000	1.00000	0.0	-0.00000	0.0	0.00000
2.0	0.5	0.1	0.1	-0.04438	0.14438	0.07781	-0.04438	-0.04438	0.06657	0.06657
2.0	0.5	0.1	0.5	-0.37575	0.47575	0.31212	-0.37575	-0.37575	0.16363	0.16363
2.0	0.5	0.1	1.0	-0.69113	0.79113	0.65444	-0.69113	-0.69113	0.13669	0.13669
2.0	0.5	0.5	0.1	0.18039	0.31961	0.19020	0.18039	0.18039	0.12941	0.12941
2.0	0.5	0.5	0.5	-0.11400	0.61400	0.44300	-0.11400	-0.11400	0.17100	0.17100
2.0	0.5	0.5	1.0	-0.39150	0.89150	0.80425	-0.39150	-0.39150	0.08726	0.08726
2.0	0.5	1.0	0.1	0.48806	0.51194	0.34403	0.48806	0.48806	0.16791	0.16791
2.0	0.5	1.0	0.5	0.23607	0.76393	0.61803	0.23607	0.23607	0.14590	0.14590
2.0	0.5	1.0	1.0	0.0	1.00000	1.00000	0.0	0.0	0.0	0.0
2.0	1.0	0.1	0.1	-0.00000	0.10000	0.10000	0.00000	-0.00000	0.09000	0.09000
2.0	1.0	0.1	0.5	-0.26667	0.36667	0.36667	-0.26667	-0.26667	0.23222	0.23222
2.0	1.0	0.1	1.0	-0.60000	0.70000	0.70000	-0.60000	-0.60000	0.21000	0.21000
2.0	1.0	0.5	0.1	0.26667	0.23333	0.23333	0.26667	0.26667	0.17889	0.17889
2.0	1.0	0.5	0.5	-0.00000	0.50000	0.50000	0.00000	-0.00000	0.25000	0.25000
2.0	1.0	0.5	1.0	-0.33333	0.83333	0.83333	-0.33333	-0.33333	0.13889	0.13889
2.0	1.0	1.0	0.1	0.60000	0.40000	0.40000	0.60000	0.60000	0.24000	0.24000
2.0	1.0	1.0	0.5	0.33333	0.66667	0.66667	0.33333	0.33333	0.22222	0.22222
2.0	1.0	1.0	1.0	-0.00000	1.00000	1.00000	0.00000	-0.00000	0.00000	0.00000
2.0	2.0	0.1	0.1	0.03701	0.06299	0.11851	0.03701	0.03701	0.11104	0.11104
2.0	2.0	0.1	0.5	-0.16416	0.26416	0.41792	-0.16416	-0.16416	0.30752	0.30752
2.0	2.0	0.1	1.0	-0.50000	0.60000	0.75000	-0.50000	-0.50000	0.30000	0.30000
2.0	2.0	0.5	0.1	0.34295	0.15705	0.27147	0.34295	0.34295	0.22884	0.22884
2.0	2.0	0.5	0.5	0.11400	0.38600	0.55700	0.11400	0.11400	0.34200	0.34200
2.0	2.0	0.5	1.0	-0.26556	0.76556	0.86722	-0.26556	-0.26556	0.20331	0.20331
2.0	2.0	1.0	0.1	0.70683	0.29317	0.45341	0.70683	0.70683	0.32049	0.32049
2.0	2.0	1.0	0.5	0.43845	0.56155	0.71922	0.43845	0.43845	0.31534	0.31534
2.0	2.0	1.0	1.0	0.0	1.00000	1.00000	0.0	0.0	0.0	0.0
2.0	10.0	0.1	0.1	0.08374	0.01626	0.14187	0.08374	0.08374	0.13956	0.13956
2.0	10.0	0.1	0.5	0.00780	0.09221	0.50390	0.00779	0.00780	0.45744	0.45744
2.0	10.0	0.1	1.0	-0.28027	0.38027	0.85987	-0.28027	-0.28027	0.53288	0.53288
2.0	10.0	0.5	0.1	0.45369	0.04631	0.32685	0.45369	0.45369	0.31171	0.31171
2.0	10.0	0.5	0.5	0.33334	0.16667	0.66667	0.33333	0.33334	0.55556	0.55556
2.0	10.0	0.5	1.0	-0.11693	0.61693	0.94154	-0.11693	-0.11693	0.36067	0.36067
2.0	10.0	1.0	0.1	0.89254	0.10746	0.54627	0.89254	0.89254	0.48757	0.48757
2.0	10.0	1.0	0.5	0.66667	0.33333	0.83333	0.66667	0.66667	0.55556	0.55556
2.0	10.0	1.0	1.0	0.0	1.00000	1.00000	0.0	0.0	0.0	0.0

ZETA	K	X	Y	R	XSTAR	YSTAR	R1	R2	E1	E2
-10.0	0.1	0.1	0.1	-0.42632	0.52632	0.10000	0.04263	0.0	0.04737	0.04737
-10.0	0.1	0.1	0.5	-0.80909	0.90909	0.50000	0.08091	0.0	0.04545	0.04545
-10.0	0.1	0.1	1.0	-0.90000	1.00000	1.00000	0.09000	0.0	0.0	0.0
-10.0	0.1	0.5	0.1	-0.02632	0.52632	0.10000	0.00263	0.0	0.04737	0.04737
-10.0	0.1	0.5	0.5	-0.40909	0.90909	0.50000	0.04091	0.0	0.04545	0.04545
-10.0	0.1	0.5	1.0	-0.50000	1.00000	1.00000	0.05000	0.0	0.0	0.0
-10.0	0.1	1.0	0.1	0.47368	0.52632	0.10000	-0.04737	0.0	0.04737	0.04737
-10.0	0.1	1.0	0.5	0.09091	0.90909	0.50000	-0.00909	0.0	0.04545	0.04545
-10.0	0.1	1.0	1.0	0.0	1.00000	1.00000	0.0	0.0	0.0	0.0
-10.0	0.5	0.1	0.1	-0.08182	0.18182	0.10000	0.00818	0.0	0.08182	0.08182
-10.0	0.5	0.1	0.5	-0.56667	0.66667	0.50000	0.05667	0.0	0.16667	0.16667
-10.0	0.5	0.1	1.0	-0.90000	1.00000	1.00000	0.09000	0.0	0.0	0.0
-10.0	0.5	0.5	0.1	0.31818	0.18182	0.10000	-0.03182	0.0	0.08182	0.08182
-10.0	0.5	0.5	0.5	-0.16667	0.66667	0.50000	0.01667	0.0	0.16667	0.16667
-10.0	0.5	0.5	1.0	-0.50000	1.00000	1.00000	0.05000	0.0	0.0	0.0
-10.0	0.5	1.0	0.1	0.81818	0.18182	0.10000	-0.08182	0.0	0.08182	0.08182
-10.0	0.5	1.0	0.5	0.33333	0.66667	0.50000	-0.03333	0.0	0.16667	0.16667
-10.0	0.5	1.0	1.0	0.0	1.00000	1.00000	0.0	0.0	0.0	0.0
-10.0	1.0	0.1	0.1	0.0	0.10000	0.10000	0.0	0.0	0.09000	0.09000
-10.0	1.0	0.1	0.5	-0.40000	0.50000	0.50000	0.04000	0.0	0.25000	0.25000
-10.0	1.0	0.1	1.0	-0.90000	1.00000	1.00000	0.09000	0.0	0.0	0.0
-10.0	1.0	0.5	0.1	0.40000	0.10000	0.10000	-0.04000	0.0	0.09000	0.09000
-10.0	1.0	0.5	0.5	0.0	0.50000	0.50000	0.0	0.0	0.25000	0.25000
-10.0	1.0	0.5	1.0	-0.50000	1.00000	1.00000	0.05000	0.0	0.0	0.0
-10.0	1.0	1.0	0.1	0.90000	0.10000	0.10000	-0.09000	0.0	0.09000	0.09000
-10.0	1.0	1.0	0.5	0.50000	0.50000	0.50000	-0.05000	0.0	0.25000	0.25000
-10.0	1.0	1.0	1.0	0.0	1.00000	1.00000	0.0	0.0	0.0	0.0
-10.0	2.0	0.1	0.1	0.04737	0.05263	0.10000	-0.00474	0.0	0.09474	0.09474
-10.0	2.0	0.1	0.5	-0.23333	0.33333	0.50000	0.02333	0.0	0.33333	0.33333
-10.0	2.0	0.1	1.0	-0.90000	1.00000	1.00000	0.09000	0.0	0.0	0.0
-10.0	2.0	0.5	0.1	0.44737	0.05263	0.10000	-0.04474	0.0	0.09474	0.09474
-10.0	2.0	0.5	0.5	0.16667	0.33333	0.50000	-0.01667	0.0	0.33333	0.33333
-10.0	2.0	0.5	1.0	-0.50000	1.00000	1.00000	0.05000	0.0	0.0	0.0
-10.0	2.0	1.0	0.1	0.94737	0.05263	0.10000	-0.09474	0.0	0.09474	0.09474
-10.0	2.0	1.0	0.5	0.66667	0.33333	0.50000	-0.06667	0.0	0.33333	0.33333
-10.0	2.0	1.0	1.0	0.0	1.00000	1.00000	0.0	0.0	0.0	0.0
-10.0	10.0	0.1	0.1	0.08901	0.01099	0.10000	-0.00890	0.0	0.09890	0.09890
-10.0	10.0	0.1	0.5	0.00909	0.09091	0.50000	-0.00091	0.0	0.45455	0.45455
-10.0	10.0	0.1	1.0	-0.90000	1.00000	1.00000	0.09000	0.0	0.0	0.0
-10.0	10.0	0.5	0.1	0.48901	0.01099	0.10000	-0.04890	0.0	0.09890	0.09890
-10.0	10.0	0.5	0.5	0.40909	0.09091	0.50000	-0.04091	0.0	0.45455	0.45455
-10.0	10.0	0.5	1.0	-0.50000	1.00000	1.00000	0.05000	0.0	0.0	0.0
-10.0	10.0	1.0	0.1	0.98901	0.01099	0.10000	-0.09890	0.0	0.09890	0.09890
-10.0	10.0	1.0	0.5	0.90909	0.09091	0.50000	-0.09091	0.0	0.45455	0.45455
-10.0	10.0	1.0	1.0	0.0	1.00000	1.00000	0.0	0.0	0.0	0.0

APPENDIX 5D

PROGRAM LISTING - IXVK

```
C
C                                IXVK
C
C     ION EXCHANGE MODEL,VARIABLE SEPARATION FACTOR
C
C    PURPOSE
C
C      TO CALCULATE FIXED BED ION EXCHANGE COLUMN BREAKTHROUGH CURVES
C
C      THE EQUATIONS SOLVED ARE
C            DX/DN & DY/DT = 0
C                    DY/DT = R
C                            = AMDA * (YSTAR - Y)
C                            = MU * (X - XSTAR)
C
C      NOTE AMDA=SIGMA,MU=RO
C
C      BASIS ON SIDE WITH LESSER NUMBER OF TRANSFER UNITS
C
C      VALUES OF THE SEPARATION FACTOR ARE HELD IN THE ARRAY SEPFAC IN
C      THE BLOCK COMMON AREA KVAL,EQUALLY SPACED AT 0.0(0.05)1.0 IN XSTAR
C
C    USAGE
C
C      THE SEPARATION FACTOR PROFILE ARRAY IS READ
C
C          READ(5,94)SEPFAK
C       94 FORMAT(16F5.4)
C
C      READ IN PARAMETERS FOR EACH BREAKTHROUGH CURVE
C
C          READ(5,100) ZETA,EK,PEND,QEND,DERP,DERQ,NINCP,NINCQ,LPUN
C      100 FORMAT(6E10.4,2I4,L4)
C
C      ZETA = MECHANISM PARAMETER
C          IF ZETA INFINITE,PUT TO -10.0
C      EK = EQUILIBRIUM RATIO,NO FUNCTION EXCEPT OUTPUT DOCUMENTATION
C      PEND,QEND = GREATEST VALUE OF N,T REQUIRED
C      DERP,DERQ = STEP SIZE IN N,T RESPECTIVELY
C      NINCQ=GOPRIN,THE LOWER VALUE OF N AT WHICH PRINTING SHOULD START
C      NINCP = PRINT INTERVAL IN N IN MULTIPLES OF DERP
C      LPUN = .TRUE. IF RESULTS TO BE PUNCHED
C
C    SUBPROGRAMS REQUIRED
C
C      AREA     NUMERICAL INTEGRATION-LISTED IN APPENDIX 5B
C      FK       TO INTERPOLATE A VALUE OF K FROM SEPFAC
C      KLOCK    TIME OF DAY IN SECONDS
C      RATE     TO CALCULATE RATE,ALLOWING FOR VARIABLE SEPARATION FACTOR
```

```
      C
0001        COMMON ZETA,EK,RZETA,RZETAP,FAC1,FAC2,AMDA,LINEAR,LIMIT,XSTAR,
           1YSTAR
0002        COMMON /KVAL/SEPFAK(21)
0003        DIMENSION X(1505),Y(1505),R(1505),Q(1505)
0004        DIMENSION XST(1505),YST(1505)
0005        LOGICAL LPUN,LINEAR,LIMIT
      C
      C     READ SEPARATION FACTOR PROFILE
      C
0006        READ(5,94)SEPFAK
0007     94 FORMAT(16F5.4)
      C
      C     READ DATA
      C
0008      1 READ(5,100) ZETA,EK,PEND,QEND,DERP,DERQ,NINCP,NINCQ,LPUN
0009    100 FORMAT(6E10.4,2I4,L4)
      C
      C     INITIALISATION TO START OF CALCULATION
0010        WRITE(6,101)
0011    101 FORMAT(1H1,45X,'ION EXCHANGE MODEL IXVK'///)
0012        IF(LPUN)WRITE(7,110)ZETA,EK,PEND,QEND,DERP,DERQ,NINCP,NINCQ
0013    110 FORMAT('99900 ION EXCHANGE MODEL IXVK'/
           1'99901'6F10.5,2I4,L4)
0014        IP=1
0015        NP=PEMD/DERP+1
0016        NQ=QEND/DERQ+1
0017        IGO=1
0018        NLEV=0
0019        NQP1=NQ+1
0020        NPP1=NP+1
0021        IXTIME=KLOCK(3)
0022        GOPRIN=NINCQ
0023        WRITE(6,102) ZETA,EK,DERP,DERQ
0024    102 FORMAT(' MECHANISM PARAMETER =',G12.5/' EQUILIBRIUM RATIO =',G12.5
           1/' STEP SIZE IN N =',G12.5/' STEP SIZE IN T =',G12.5,60X,G10.4)
0025        WRITE(6,93)SEPFAK
0026     93 FORMAT('0SEPARATION FACTOR PROFILE'/(11G12.4))
      C
      C     DECISION ON BASIS
0027        IF(ZETA-1.0002)50,50,51
      C
      C     PARTICLE PHASE BASIS
0028     50 AMDA=1.0
0029        WRITE(6,126)
0030    126 FORMAT(' N AND T(IE ZN) ARE BASED ON NUMBER OF PARTICLE PHASE TRAN
           1SFER UNITS')
0031        GO TO 52
      C
```

```
                C     SOLUTION PHASE BASIS
0032               51 AMDA=ZETA
0033                  WRITE(6,107)
0034              107 FORMAT(' N AND T(IE ZN) ARE BASED ON NUMBER OF SOLUTION PHASE TRAN
                     1SFER UNITS')
                C
                C     SET UP COMMON VARIABLES FOR USE IN RATE FUNCTION
0035               52 RZETA=1.0/ZETA
0036                  LIMIT=.FALSE.
0037                  IF(ZETA.LT.0.0001)LIMIT=.TRUE.
0038                  IF(EK.LT.0.9998.OR.EK.GT.1.0002) GO TO 56
                C
                C     LINEAR EQUILIBRIUM
0039                  FAC1=1.0
0040                  FAC2=1.0
0041                  LINEAR=.TRUE.
0042                  GO TO 57
                C     NON LINEAR EQUILIBRIUM
0043               56 FAC2=ZETA*(EK-1.0)
0044                  FAC1=(1.0+EK*ZETA)/FAC2
0045                  FAC2=EK/FAC2
0046                  LINEAR=.FALSE.
0047               57 RZETAP=1.0/(ZETA+1.0)
                C                                                    )5,ADMA,ATEZ(PMUDP LLAC
                C
                C     CALCULATION ALONG IP=1
                C
0048                  X(1)=1.0
0049                  Y(1)=0.0
0050                  R(1)=RATE(1.0,0.0)
0051                  Q(1)=0.0
0052                  INIL=1
0053                  DO200IQ=2,NQP1
0054                  XD=IQ
0055                  Q(IQ)=(XD-1.0)*DERQ
0056                  X(IQ)=1.0
                C
                C     CHECK THAT Y NOT 1.0
0057                  IF(Y(IQ-1).LE.0.9999) GO TO 17
0058                  Y(IQ)=1.0
0059                  R(IQ)=0.0
0060                  GO TO 200
                C
                C     RUNGE KUTTA PROCEDURE TO GET Y(IQ), NOTE X(IQ)=1.0
0061               17 YO=Y(IQ-1)
0062                  RKO=DERQ*R(IQ-1)
0063                  XD=YO+.5*RKO
0064                  RK1=DERQ*RATE(1.0,XD)
0065                  XD=YO+RK1*.5
```

```
0066              RK2=DERQ*RATE(1.0,XD)
0067              XD=Y0+RK2
0068              RK3=DERQ*RATE(1.0,XD)
0069              Y1=Y0+(RK0+2.0*(RK1+RK2)+RK3)/6.0
0070              Y(IQ)=Y1
0071              R(IQ)=RATE(1.0,Y1)
0072              ISAT=IQ
                C                                QI,PI,)QI(R,1Y,3KR,2KR,1KR,0KR,0Y)171,6(ETIRW
0073            171 FORMAT(9G14.5)
0074            200 CONTINUE
                C
                C     NOW SUCCESSIVE INCREMENTATION DOWN COLUMN
                C
0075              DO204IP=2,NPP1
0076              IF(INIL.NE.1) GO TO 12
                C
                C     INIL=1, CALCULATION OF X(1), NOTE Y(1)=0.0, USING RUNGE KUTTA
0077              X0=X(1)
0078              RK0=-DERP*R(1)
0079              XD=X0+RK0*.5
0080              RK1=-DERP*RATE(XD,0.0)
0081              XD=X0+RK1*.5
0082              RK2=-DERP*RATE(XD,0.0)
0083              XD=X0+RK2
0084              RK3=-DERP*RATE(XD,0.0)
0085              X1=X0+(RK0+RK3+2.0*(RK1+RK2))/6.0
0086              X(1)=X1
0087              R(1)=RATE(X1,0.0)
0088              XST(1)=XSTAR
0089              YST(1)=YSTAR
0090              JSAT=2
                C                                 QI,PI,)1(R,1X,3KR,2KR,1KR,0KR,0X)171,6(ETIRW
0091              GO TO 6
                C
                C     CALCULATION OF OTHER X,Y AT THIS LEVEL OF P
0092             12 JSAT=INIL
0093              6 DO201IQ=JSAT,NQP1
0094              X1=X(IQ-1)
0095              Y1=Y(IQ-1)
0096              R1=R(IQ-1)
0097              X2=X(IQ)
0098              Y2=Y(IQ)
0099              R2=R(IQ)
                C
                C     CALCULATE FIRST ESTIMATES OF X,Y AT NEW POINT
0100              XD=X2-R2*DERP
0101              YD=Y1+R1*DERQ
                C
                C     CHECK THAT X,Y NOT LESS THAN .0001
```

```
0102            IF(XD+YD.GT.0.0001) GO TO 21
                C     COLUMN STILL EMPTY
0103            X(IQ)=0.0
0104            Y(IQ)=0.0
0105            R(IQ)=0.0
0106            XST(IQ)=0.0
0107            YST(IQ)=0.0
0108            INIL=IQ
0109            GOTO201
                C
                C     CHECK THAT X,Y NOT GREATER THAN .9999
0110          21 IF(XD+YD.LT.1.9999) GO TO 22
                C     COLUMN SATURATED, BRANCH OUT OF LOOP
0111            X(IQ)=1.0
0112            Y(IQ)=1.0
0113            R(IQ)=0.0
0114            XST(IQ)=1.0
0115            YST(IQ)=1.0
0116            ISAT=IQ
0117            GOTO13
                C
                C     CALCULATION OF SECOND ESTIMATES OF X,Y AT THIS POINT
0118          22 RD=RATE(XD,YD)
0119            XDD=X2-RD*DERP
0120            YDD=Y1+RD*DERQ
                C
                C     CALCULATION OF FINAL VALUES OF X,Y AT THIS POINT
0121            X2=0.5*(XD+XDD)
0122            X(IQ)=X2
0123            Y2=0.5*(YD+YDD)
0124            Y(IQ)=Y2
0125            R(IQ)=RATE(X2,Y2)
0126            XST(IQ)=XSTAR
0127            YST(IQ)=YSTAR
                C
                C     CHECK X IN ACCEPTABLE RANGE
0128            IF(ABS(X2-.5).LE.0.501)GOTO201
                C     X OUTSIDE RANGE
0129            WRITE(6,108)
0130          108 FORMAT(' SOLUTION CONCENTRATION NOT IN ACCEPTABLE RANGE')
0131            NAMELIST/XOUT/IP,IQ,X,Y,R
0132            WRITE(6,XOUT)
0133            GO TO 59
0134          201 CONTINUE
                C
                C     PRINTOUT OF BREAKTHROUGH CURVES
0135           13 NLEV=NLEV+1
0136            IF(NLEV.LT.NINCP) GO TO 204
0137            NLEV=0
```

```
0138              P=IP-1
0139              P=P*DERP
0140              IF(P.LT.GOPRIN)GOTO204
0141              WRITE(6,103) P
0142          103 FORMAT(1H1,'NUMBER OF TRANSFER UNITS =',G12.5/)
0143              WRITE(6,104)
0144          104 FORMAT(3(6X'T'4X'X'6X'Y'4X'XSTAR YSTAR  RATE'))
0145              NINCQ=(ISAT-IGO+50)/100
0146              IF(NINCQ.EQ.0)NINCQ=1
0147              IGO=INIL/NINCQ*NINCQ+1
0148              WRITE(6,105)(Q(K),X(K),Y(K),XST(K),YST(K),R(K),K=IGO,ISAT,NINCQ)
0149          105 FORMAT(3(F8.2,2F7.4,3F6.3))
0150              IOUT=(ISAT-IGO)/NINCQ+1
0151              IF(LPUN)WRITE(7,111)P,IOUT
0152          111 FORMAT('99902'F10.4,I4)
0153              IF(LPUN)WRITE(7,112) (Q(K),X(K),Y(K),K=IGO,ISAT,NINCQ)
0154          112 FORMAT(('99999',5(F5.1,2F5.3)))
0155              IF(ISAT.GT.NQ)GOTO204
0156              DO210IQ=1,ISAT
0157              XST(IQ)=1.0-X(IQ)
0158          210 CONTINUE
0159              RR=AREA(XST,ISAT,DERQ)
0160              WRITE(6,127)RR
0161          127 FORMAT('0AREA'G15.5)
0162          204 CONTINUE
0163              IXTIME=KLOCK(3)-IXTIME
0164              WRITE(6,133) IXTIME
0165          133 FORMAT(////G10.4)
0166           59 GOTO1
0167              END
```

```
0001            FUNCTION RATE(X,Y)
                C
                C   PURPOSE
                C
                C
                C     TO CALCULATE RATE=DY/DT,WITH A VARIABLE SEPARATION FACTOR
                C
                C     WEGSTIEN ITERATION USED
                C
                C   SUBPROGRAMS REQUIRED
                C
                C     RATEM   TO CALCULATE DY/DT AT SOME K VALUE,EQUIVALENT TO RATE LISTED
                C     IN APPENDIX 5B
                C
                C
0002            COMMON ZETA,EK,RZETA,RZETAP,FAC1,FAC2,AMDA,LINEAR,LIMIT,XSTAR,
               1YSTAR
0003            LOGICAL PRIN
                C
                C     INITIAL ESTIMATES FOR WEGSTIEN
                C
0004            PRIN=.FALSE.
0005            EK1=EK
0006            IF(PRIN)WRITE(6,103)X,Y
0007          103 FORMAT(1H0,2G12.5/)
0008            WX0=(X+Y)/2.0
0009            EK=FK(WX0)
0010            RATE=RATEM(X,Y)
0011            WY0=XSTAR
0012            IF(PRIN)WRITE(6,102)WX0,WX1,WX2,WY0,WY1,WY2,EK,RATE,XSTAR,YSTAR,D
0013            WX1=WY0
0014            EK=FK(WX1)
0015            RATE=RATEM(X,Y)
0016            WY1=XSTAR
0017            IF(PRIN)WRITE(6,102)WX0,WX1,WX2,WY0,WY1,WY2,EK,RATE,XSTAR,YSTAR,D
0018            IF(ABS(WX1-WY1).LT.0.0001)RETURN
0019            DO200KOUNT=1,50
0020            D=(WX0-WY0)/(WX1-WY1)-1.0
0021            IF(ABS(D).LT.1.0E-20)GOTO13
0022            WX2=WX1+(WX1-WX0)/D
0023            EK=FK(WX2)
0024            RATE=RATEM(X,Y)
0025            WY2=XSTAR
0026            IF(PRIN)WRITE(6,102)WX0,WX1,WX2,WY0,WY1,WY2,EK,RATE,XSTAR,YSTAR,D
0027          102 FORMAT(1H ,11G12.5)
0028            IF(ABS(WX2-WY2).LT.0.0001)GO TO 5
0029            WX0=WX1
0030            WX1=WX2
0031            WY0=WY1
```

```
0032            WY1=WY2
0033          200 CONTINUE
0034            WRITE(6,100)X,Y,WX0,WX1,WY0,WY1
0035          100 FORMAT(' NO CONVERGENCE IN RATE AFTER 50 LOOPS'/6G15.5)
0036            STOP
0037           13 WRITE(6,101)X,Y,WX0,WX1,WY0,WY1
0038          101 FORMAT(' D ZERO IN WEGSTIEN'/6G15.5)
0039            STOP
0040            5 EK=EK1
0041            RETURN
0042            END
```



```
0001            FUNCTION FK(XSTAR)
                C
                C   PURPOSE
                C
                C     TO LINEARLY INTERPOLATE A VALUE FOR THE SEPARATION FACTOR FOR THE
                C     CURRENT VALUE OF XSTAR FROM THE ARRAY SEPFAC
                C
0002            COMMON ZETA,EK,RZETA,RZETAP,FAC1,FAC2,AMDA,LINEAR,LIMIT,XSTDD,
               1YSTAR
0003            COMMON /KVAL/SEPFAK(21)
0004            LOGICAL LINEAR,LIMIT
0005            IK=XSTAR/0.05+1
0006            IF(IK.GE.21)GOTO10
0007            P=(XSTAR-(IK-1)*0.05)/0.05
0008            FK=(1.0-P)*SEPFAK(IK)+P*SEPFAK(IK+1)
0009            GOTO11
0010         10 FK=SEPFAK(21)
                C     SET UP COMMON VARIABLES FOR USE IN RATE FUNCTION
0011         11 IF(FK.LT.0.9998.OR.FK.GT.1.0002) GO TO 56
                C
                C     LINEAR EQUILIBRIUM
0012            FAC1=1.0
0013            FAC2=1.0
0014            LINEAR=.TRUE.
0015            RETURN
                C
                C     NON LINEAR EQUILIBRIUM
0016         56 FAC2=ZETA*(FK-1.0)
0017            FAC1=(1.0+FK*ZETA)/FAC2
0018            FAC2=FK/FAC2
0019            LINEAR=.FALSE.
0020            RETURN
0021            END
```

GENERALISED BREAKTHROUGH CURVES

CHARACTERISTIC TIME VALUES

MECHANISM PARAMETER	SEPARATION FACTOR	TRANSFER UNITS	X=0.0	0.0245	0.0955	0.2061	0.3455	0.5000	0.6545	0.7939	0.9045	0.9755	1.0000
0.0	0.1	10.0	0.0	0.0	0.0	0.1	1.0	2.7	5.9	13.0	30.8	71.5	126.0
		20.0	0.0	0.0	0.3	1.3	3.1	6.1	12.1	25.5	59.7	139.1	217.0
		30.0	0.0	0.0	1.0	2.7	5.2	9.5	18.1	38.0	88.9	206.6	277.0
		40.0	0.0	0.4	1.9	4.1	7.3	12.9	24.2	50.3	118.5	269.6	340.0
		50.0	0.0	0.8	2.9	5.4	9.4	16.3	30.2	62.8	147.0	283.1	330.0
		60.0	0.0	1.5	3.8	6.9	11.5	19.6	36.2	75.1	176.3	317.1	364.0
		70.0	0.1	2.2	4.8	8.3	13.7	23.0	42.2	87.4	205.0	347.1	394.0
		80.0	0.2	2.8	5.9	9.8	15.8	26.4	48.1	99.9	235.0	377.1	424.0
		90.0	0.3	3.5	6.9	11.3	17.9	29.7	54.1	111.9	261.0	403.1	450.0
		100.0	0.6	4.3	8.0	12.7	20.0	33.1	60.1	124.5	287.0	429.1	476.0
	0.5	10.0	0.0	0.7	2.1	3.7	5.7	8.2	11.4	15.6	21.0	28.4	41.5
		20.0	1.0	3.6	6.3	9.2	12.7	17.1	22.7	29.9	38.8	49.8	68.0
		30.0	3.0	7.1	11.0	15.0	19.9	26.0	33.9	43.9	56.1	70.8	92.1
		40.0	6.0	11.0	15.9	21.0	27.1	34.9	45.1	57.9	73.2	91.3	116.1
		50.0	9.0	15.1	20.8	27.0	34.4	43.9	56.3	71.8	90.3	111.2	138.4
		60.0	12.0	19.3	25.9	33.0	41.6	52.8	67.3	85.6	107.1	131.2	162.2
		70.0	14.6	23.6	31.1	39.0	48.9	61.7	78.5	99.6	124.1	151.2	184.5
		80.0	18.0	27.9	36.2	45.2	56.2	70.7	89.6	113.4	141.0	171.0	203.0
		90.0	22.0	32.3	41.5	51.2	63.5	79.6	100.8	127.3	157.8	191.0	213.0
		100.0	26.0	36.8	46.7	57.4	70.8	88.5	111.7	140.9	174.6	210.4	226.0
	0.8	10.0	0.0	2.0	3.7	5.4	7.2	9.2	11.5	14.2	17.5	22.3	32.0
		20.0	3.2	7.0	10.1	13.0	15.9	19.1	22.6	26.5	31.3	37.9	50.5
		30.0	7.6	12.8	17.1	20.9	24.8	28.9	33.5	38.6	44.6	52.7	67.5
		40.0	12.5	19.2	24.3	29.0	33.8	38.8	44.3	50.5	57.6	67.1	83.1
		50.0	17.5	25.7	31.7	37.2	42.7	48.6	55.1	62.2	70.5	81.1	99.1
		60.0	23.5	32.3	39.3	45.5	51.8	58.6	65.9	73.9	83.2	94.9	114.1
		70.0	29.2	39.1	46.9	53.8	60.9	68.4	76.6	85.6	95.7	108.5	129.1
		80.0	35.2	46.0	54.6	62.2	69.9	78.3	87.3	97.2	108.3	122.1	144.4
		90.0	41.2	53.0	62.3	70.6	79.1	88.1	98.0	108.8	120.7	135.5	159.2
		100.0	47.2	60.1	70.1	79.0	88.2	98.0	108.7	120.4	133.3	149.0	172.9
	1.0	10.0	0.8	2.8	4.6	6.2	7.8	9.5	11.3	13.4	16.1	20.2	28.6
		20.0	4.7	9.1	12.2	14.7	17.1	19.5	22.1	25.0	28.6	33.9	44.5
		30.0	10.6	16.3	20.3	23.5	26.5	29.5	32.6	36.2	40.5	46.6	59.0
		40.0	17.1	23.9	28.7	32.5	36.0	39.5	43.1	47.1	52.0	59.1	72.5
		50.0	23.5	31.8	37.3	41.7	45.6	49.5	53.5	58.0	63.4	71.1	85.2
		60.0	30.5	39.9	46.1	50.9	55.2	59.5	63.9	68.8	74.7	82.9	98.1
		70.0	38.2	48.3	54.9	60.2	64.9	69.5	74.3	79.5	85.8	94.6	111.1
		80.0	45.5	56.7	63.8	69.5	74.6	79.5	84.6	90.2	96.9	106.3	123.1
		90.0	53.5	65.1	72.8	78.8	84.2	89.5	94.9	100.8	107.9	117.9	136.1
		100.0	61.2	73.7	81.9	88.3	93.9	99.5	105.2	111.4	118.9	129.2	148.1
	1.2	10.0	1.5	3.6	5.4	6.8	8.2	9.6	11.1	12.9	15.2	18.7	26.5
		20.0	6.7	11.0	13.7	15.9	17.8	19.6	21.6	23.9	26.7	31.2	40.5
		30.0	13.6	19.3	22.7	25.3	27.5	29.7	31.9	34.5	37.8	42.8	53.0
		40.0	21.6	27.9	31.9	34.8	37.3	39.7	42.1	44.9	48.5	53.9	65.5
		50.0	29.6	36.9	41.4	44.5	47.1	49.7	52.3	55.3	59.1	64.9	77.0
		60.0	38.1	46.2	50.9	54.2	57.0	59.7	62.5	65.6	69.6	75.8	88.5
		70.0	47.0	55.4	60.5	64.0	66.9	69.7	72.6	75.8	80.0	86.4	99.5
		80.0	56.0	64.9	70.2	73.8	76.8	79.7	82.7	86.0	90.3	96.9	110.5
		90.0	65.0	74.4	79.9	83.6	86.8	89.7	92.7	96.2	100.5	107.4	121.5
		100.0	73.5	84.1	89.7	93.5	96.7	99.7	102.8	106.3	110.8	117.7	132.1
	2.0	10.0	3.5	5.9	7.1	8.1	8.9	9.7	10.6	11.7	13.3	15.9	21.6
		20.0	12.5	15.5	16.9	17.9	18.8	19.7	20.7	21.9	23.5	26.3	32.6
		30.0	22.2	25.4	26.9	27.9	28.8	29.7	30.7	31.9	33.6	36.4	43.1
		40.0	32.2	35.4	36.9	37.9	38.8	39.7	40.7	41.9	43.6	46.5	53.1
		50.0	42.2	45.4	46.9	47.9	48.8	49.7	50.7	51.9	53.6	56.5	63.1
		60.0	52.2	55.4	56.9	57.9	58.8	59.7	60.7	61.9	63.6	66.5	73.1
		70.0	62.2	65.4	66.9	67.9	68.8	69.7	70.7	71.9	73.6	76.5	83.1
		80.0	72.2	75.4	76.9	77.9	78.8	79.7	80.7	81.9	83.6	86.5	93.1
		90.0	82.2	85.4	86.9	87.9	88.8	89.7	90.7	91.9	93.6	96.5	103.1
		100.0	92.2	95.4	96.9	97.9	98.8	99.7	100.7	101.9	103.6	106.5	113.1
	10.0	10.0	8.2	8.6	8.9	9.1	9.4	9.7	10.1	10.7	11.6	13.1	17.0
		20.0	18.2	18.6	18.9	19.1	19.4	19.7	20.1	20.7	21.6	23.1	27.0
		30.0	28.2	28.6	28.9	29.1	29.4	29.7	30.2	30.8	31.6	33.1	37.0
		40.0	38.2	38.6	38.9	39.1	39.4	39.7	40.2	40.8	41.6	43.2	47.0
		50.0	48.2	48.6	48.9	49.1	49.4	49.7	50.2	50.8	51.6	53.2	57.0
		60.0	58.2	58.6	58.9	59.1	59.4	59.7	60.2	60.8	61.6	63.2	67.0
		70.0	68.2	68.6	68.9	69.1	69.4	69.7	70.2	70.8	71.7	73.2	77.0
		80.0	78.2	78.6	78.9	79.1	79.4	79.7	80.2	80.8	81.7	83.2	87.0
		90.0	88.2	88.7	88.9	89.1	89.4	89.8	90.2	90.8	91.7	93.2	97.0
		100.0	98.2	98.7	98.9	99.2	99.4	99.8	100.2	100.8	101.7	103.2	107.0

GENERALISED BREAKTHROUGH CURVES

CHARACTERISTIC TIME VALUES

MECHANISM PARAMETER	SEPARATION FACTOR	TRANSFER UNITS	X=0.0	0.0245	0.0955	0.2061	0.3455	0.5000	0.6545	0.7939	0.9045	0.9755	1.0000
0.1	0.1	10.0	0.0	0.0	0.0	0.1	1.0	2.6	5.7	12.7	30.2	72.8	139.5
		20.0	0.0	0.0	0.2	1.3	3.0	6.0	11.9	25.3	59.7	141.1	219.0
		30.0	0.0	0.0	1.0	2.6	5.1	9.4	18.0	37.7	88.5	207.6	278.0
		40.0	0.0	0.0	0.4	1.9	4.0	7.2	12.8	24.1	50.0	117.5	245.1	292.0
		50.0	0.0	0.0	0.8	2.8	5.4	9.3	16.2	30.1	62.4	147.1	283.1	330.0
		60.0	0.0	0.0	1.5	3.8	6.8	11.4	19.5	36.1	74.9	175.0	315.1	362.0
		70.0	0.1	0.2	2.2	4.8	8.3	13.6	22.9	42.1	87.3	205.0	347.1	394.0
		80.0	0.2	0.2	2.7	5.8	9.7	15.7	26.3	47.9	99.4	233.0	375.1	422.0
		90.0	0.4	0.4	3.5	6.8	11.2	17.8	29.6	53.9	111.9	261.0	403.1	450.0
		100.0	0.6	0.6	4.2	7.9	12.6	19.9	32.9	59.9	123.9	287.0	429.1	476.0
	0.5	10.0	0.0	0.6	1.9	3.5	5.5	8.0	11.3	15.6	21.3	29.2	44.0
		20.0	1.0	3.4	6.1	9.0	12.5	16.9	22.6	29.9	39.2	51.2	70.1
		30.0	3.0	6.9	10.7	14.8	19.7	25.8	33.8	44.0	56.6	72.3	96.1
		40.0	5.0	10.7	15.6	20.7	26.9	34.7	45.0	58.0	73.8	92.8	120.2
		50.0	7.5	14.7	20.5	26.6	34.1	43.7	56.1	72.0	90.7	113.3	144.1
		60.0	11.2	18.9	25.5	32.7	41.4	52.6	67.2	85.8	107.9	133.2	166.6
		70.0	14.0	23.1	30.7	38.7	48.6	61.5	78.3	99.6	124.7	153.0	188.5
		80.0	18.0	27.4	35.9	44.8	56.0	70.4	89.5	113.6	141.5	172.9	204.0
		90.0	22.0	31.9	41.1	50.9	63.2	79.3	100.6	127.3	158.5	192.9	215.0
		100.0	26.0	36.3	46.3	57.0	70.5	88.3	111.7	141.2	175.4	212.4	228.0
	0.8	10.0	0.0	1.8	3.5	5.2	7.1	9.1	11.5	14.3	17.8	22.9	33.5
		20.0	2.7	6.7	9.8	12.7	15.7	19.0	22.6	26.7	31.8	38.9	52.5
		30.0	7.1	12.4	16.7	20.6	24.6	28.8	33.5	38.8	45.2	53.9	70.0
		40.0	11.5	18.6	23.9	28.6	33.5	38.7	44.4	50.7	58.2	68.2	86.1
		50.0	16.5	25.1	31.2	36.8	42.5	48.5	55.2	62.5	71.1	82.5	102.1
		60.0	22.5	31.6	38.7	45.1	51.5	58.4	65.9	74.3	83.9	96.5	117.1
		70.0	28.2	38.4	46.3	53.3	60.6	68.3	76.7	86.0	96.6	110.1	132.1
		80.0	33.7	45.3	54.0	61.7	69.6	78.2	87.4	97.6	109.1	123.9	147.2
		90.0	39.7	52.2	61.6	70.1	78.7	88.0	98.1	109.2	121.7	137.4	162.2
		100.0	45.7	59.2	69.4	78.5	87.8	97.9	108.9	120.8	134.2	150.9	177.2
	1.0	10.0	0.5	2.5	4.4	6.0	7.7	9.4	11.4	13.6	16.4	20.7	29.6
		20.0	4.2	8.7	11.8	14.4	16.9	19.4	22.1	25.2	29.0	34.6	46.0
		30.0	9.7	15.8	19.8	23.2	26.3	29.4	32.7	36.4	41.0	47.6	60.5
		40.0	16.1	23.2	28.2	32.2	35.8	39.4	43.2	47.5	52.6	60.1	74.5
		50.0	22.5	31.1	36.7	41.2	45.4	49.4	53.7	58.4	64.1	72.1	87.2
		60.0	29.5	39.1	45.4	50.4	55.0	59.4	64.1	69.2	75.4	84.1	100.1
		70.0	36.5	47.3	54.2	59.6	64.6	69.4	74.5	80.0	86.6	95.9	113.1
		80.0	44.2	55.5	63.1	69.0	74.3	79.4	84.8	90.7	97.7	107.6	126.1
		90.0	52.2	63.9	72.0	78.3	83.9	89.4	95.1	101.4	108.8	119.2	138.1
		100.0	59.2	72.5	81.0	87.7	93.6	99.4	105.4	111.9	119.8	130.8	151.1
	1.2	10.0	1.0	3.2	5.1	6.6	8.1	9.6	11.2	13.1	15.5	19.2	27.5
		20.0	6.1	10.5	13.4	15.6	17.6	19.6	21.7	24.1	27.1	31.8	41.5
		30.0	12.6	18.6	22.2	24.9	27.3	29.6	32.0	34.8	38.3	43.4	54.5
		40.0	20.1	27.1	31.4	34.5	37.1	39.7	42.3	45.3	49.0	54.8	67.0
		50.0	28.1	36.1	40.7	44.1	47.0	49.7	52.5	55.7	59.7	65.7	78.5
		60.0	36.6	45.2	50.2	53.8	56.8	59.7	62.6	66.0	70.2	76.6	90.0
		70.0	45.1	54.4	59.7	63.5	66.7	69.7	72.8	76.2	80.6	87.4	101.5
		80.0	53.5	63.8	69.4	73.3	76.6	79.7	82.9	86.4	91.0	97.9	112.2
		90.0	62.5	73.2	79.1	83.1	86.5	89.7	93.0	96.6	101.3	108.5	123.1
		100.0	71.5	82.7	88.8	93.0	96.4	99.7	103.0	106.8	111.6	118.9	134.1
	2.0	10.0	3.0	5.4	6.9	7.9	8.8	9.7	10.7	11.9	13.5	16.1	22.1
		20.0	11.2	14.9	16.6	17.8	18.7	19.7	20.8	22.1	23.8	26.7	33.1
		30.0	21.1	24.8	26.5	27.7	28.7	29.7	30.8	32.1	33.9	36.8	43.6
		40.0	30.7	34.7	36.5	37.7	38.7	39.7	40.8	42.1	43.9	46.9	53.6
		50.0	40.7	44.7	46.5	47.7	48.7	49.7	50.8	52.1	53.9	56.9	63.6
		60.0	50.7	54.7	56.5	57.7	58.7	59.7	60.8	62.1	63.9	66.9	73.6
		70.0	60.7	64.7	66.5	67.7	68.7	69.7	70.8	72.1	73.9	76.9	83.6
		80.0	70.7	74.7	76.5	77.7	78.7	79.7	80.8	82.1	83.9	86.9	93.6
		90.0	80.7	84.7	86.5	87.7	88.7	89.7	90.8	92.1	93.9	96.9	103.6
		100.0	90.7	94.7	96.5	97.7	98.7	99.7	100.8	102.1	103.9	106.9	113.6
	10.0	10.0	7.6	8.4	8.8	9.1	9.4	9.7	10.2	10.8	11.7	13.2	17.0
		20.0	17.6	18.4	18.8	19.1	19.4	19.7	20.2	20.8	21.7	23.2	27.0
		30.0	27.6	28.4	28.8	29.1	29.4	29.7	30.2	30.8	31.7	33.2	37.0
		40.0	37.6	38.4	38.8	39.1	39.4	39.7	40.2	40.8	41.7	43.2	47.0
		50.0	47.6	48.4	48.8	49.1	49.4	49.7	50.2	50.8	51.7	53.2	57.0
		60.0	57.6	58.4	58.8	59.1	59.4	59.7	60.2	60.8	61.7	63.2	67.0
		70.0	67.6	68.4	68.8	69.1	69.4	69.7	70.2	70.8	71.7	73.2	77.0
		80.0	77.6	78.4	78.8	79.1	79.4	79.7	80.2	80.8	81.7	83.2	87.2
		90.0	87.6	88.4	88.8	89.1	89.4	89.7	90.2	90.8	91.7	93.2	97.2
		100.0	97.6	98.4	98.8	99.1	99.4	99.7	100.2	100.8	101.7	103.2	107.2

GENERALISED BREAKTHROUGH CURVES

CHARACTERISTIC TIME VALUES

MECHANISM PARAMETER	SEPARATION FACTOR	TRANSFER UNITS	X=0.0	0.0245	0.0955	0.2061	0.3455	0.5000	0.6545	0.7939	0.9045	0.9755	1.0000
0.3	0.1	10.0	0.0	0.0	0.0	0.0	0.8	2.4	5.5	12.3	29.9	75.1	162.0
		20.0	0.0	0.0	0.2	1.2	2.9	5.8	11.6	24.8	59.1	143.1	231.0
		30.0	0.0	0.0	0.9	2.5	5.0	9.2	17.6	37.2	87.6	209.6	280.0
		40.0	0.0	0.3	1.8	3.9	7.0	12.6	23.7	49.7	116.3	245.1	292.0
		50.0	0.0	0.8	2.7	5.3	9.1	15.9	29.7	62.0	145.3	281.1	328.0
		60.0	0.0	1.3	3.7	6.7	11.2	19.3	35.6	74.3	175.0	315.1	362.0
		70.0	0.1	2.1	4.7	8.1	13.4	22.6	41.7	86.4	199.5	270.5	294.0
		80.0	0.2	2.7	5.7	9.6	15.5	26.0	47.7	98.6	233.0	375.1	422.0
		90.0	0.3	3.4	6.7	11.0	17.6	29.4	53.6	111.3	261.0	403.1	450.0
		100.0	0.6	4.2	7.8	12.5	19.7	32.7	59.6	123.1	240.5	311.5	335.0
	0.5	10.0	0.0	0.0	1.7	3.2	5.2	7.8	11.2	15.7	21.9	30.9	48.5
		20.0	0.5	3.0	5.7	8.6	12.1	16.6	22.5	30.1	39.9	53.5	76.1
		30.0	2.0	6.4	10.2	14.3	19.2	25.5	33.6	44.2	57.4	74.8	103.0
		40.0	4.5	10.1	15.0	20.2	26.4	34.4	44.8	58.2	74.7	95.8	127.6
		50.0	7.5	14.0	19.9	26.1	33.6	43.3	56.0	72.1	91.9	116.2	151.6
		60.0	10.0	18.1	24.9	32.1	40.9	52.2	67.0	86.0	109.0	136.3	176.1
		70.0	14.0	22.2	30.0	38.1	48.1	61.1	78.2	100.0	126.1	157.0	198.2
		80.0	16.0	26.6	35.1	44.2	55.4	70.0	89.3	113.8	142.8	176.9	210.0
		90.0	20.0	30.9	40.3	50.3	62.6	78.9	100.4	127.5	159.8	196.9	220.0
		100.0	24.0	35.2	45.4	56.3	69.9	87.9	111.4	141.5	176.5	215.7	231.3
	0.8	10.0	0.0	1.4	3.1	4.9	6.8	9.0	11.5	14.5	18.4	24.3	36.0
		20.0	2.2	6.0	9.2	12.2	15.4	18.8	22.6	27.1	32.6	40.4	56.0
		30.0	6.0	11.5	16.0	20.0	24.2	28.6	33.6	39.3	46.2	55.6	73.1
		40.0	10.5	17.5	23.0	28.0	33.0	38.5	44.5	51.3	59.5	70.5	90.1
		50.0	15.5	23.8	30.3	36.1	42.0	48.3	55.3	63.2	72.4	84.8	107.0
		60.0	20.5	30.3	37.7	44.3	51.0	58.2	66.1	75.0	85.3	98.8	123.0
		70.0	26.2	36.9	45.1	52.5	60.0	68.0	76.8	86.7	98.1	113.0	138.2
		80.0	32.2	43.6	52.7	60.8	69.0	77.9	87.6	98.4	110.8	126.8	153.2
		90.0	38.2	50.5	60.3	69.1	78.1	87.7	98.3	110.0	123.4	140.4	168.2
		100.0	44.2	57.4	68.0	77.5	87.2	97.6	109.1	121.6	135.9	154.3	183.2
	1.0	10.0	0.0	2.1	3.9	5.7	7.4	9.3	11.4	13.9	17.0	21.8	32.0
		20.0	3.5	7.8	11.1	13.9	16.6	19.3	22.3	25.6	29.8	35.9	49.0
		30.0	8.6	14.7	19.0	22.6	25.9	29.3	32.9	37.0	42.0	49.1	64.0
		40.0	14.5	21.9	27.2	31.4	35.4	39.3	43.5	48.1	53.8	61.9	77.2
		50.0	20.5	29.5	35.6	40.5	44.9	49.3	54.0	59.1	65.3	74.4	91.1
		60.0	27.5	37.4	44.2	49.6	54.5	59.3	64.4	70.0	76.8	86.3	105.1
		70.0	34.2	45.4	52.9	58.7	64.1	69.3	74.8	80.8	88.1	98.3	118.1
		80.0	41.2	53.5	61.7	68.0	73.7	79.3	85.1	91.6	99.3	110.2	131.1
		90.0	49.2	61.9	70.5	77.3	83.4	89.3	95.5	102.3	110.4	121.9	143.1
		100.0	56.3	70.1	79.4	86.6	93.0	99.3	105.8	113.0	121.5	133.5	156.1
	1.2	10.0	0.5	2.7	4.6	6.3	7.9	9.5	11.3	13.4	16.0	20.2	29.0
		20.0	4.7	9.5	12.6	15.1	17.4	19.6	21.9	24.5	27.9	32.9	44.0
		30.0	11.1	17.3	21.3	24.4	27.0	29.6	32.3	35.3	39.1	44.9	57.5
		40.0	18.1	25.7	30.4	33.8	36.8	39.6	42.6	45.9	50.1	56.4	70.0
		50.0	26.0	34.3	39.6	43.4	46.6	49.7	52.8	56.4	60.8	67.6	82.0
		60.0	33.5	43.2	49.0	53.0	56.4	59.7	63.0	66.7	71.4	78.7	93.1
		70.0	41.5	52.4	58.4	62.7	66.3	69.7	73.2	77.1	82.0	89.5	104.2
		80.0	50.2	61.5	68.0	72.5	76.2	79.7	83.3	87.3	92.4	100.1	116.1
		90.0	59.2	70.9	77.6	82.2	86.1	89.7	93.4	97.6	102.8	110.9	127.1
		100.0	68.2	80.2	87.3	92.0	96.0	99.7	103.5	107.8	113.1	121.4	138.1
	2.0	10.0	1.7	4.7	6.4	7.6	8.7	9.7	10.9	12.2	13.9	16.8	23.6
		20.0	9.6	13.9	16.0	17.4	18.6	19.8	21.0	22.4	24.3	27.5	34.6
		30.0	18.8	23.6	25.9	27.4	28.6	29.8	31.0	32.5	34.4	37.6	45.1
		40.0	28.6	33.5	35.9	37.4	38.6	39.8	41.0	42.5	44.5	47.7	55.1
		50.0	38.6	43.5	45.9	47.3	48.6	49.8	51.0	52.5	54.5	57.7	65.6
		60.0	48.6	53.5	55.8	57.3	58.6	59.8	61.0	62.5	64.5	67.7	75.6
		70.0	58.6	63.5	65.8	67.3	68.6	69.8	71.0	72.5	74.5	77.7	85.6
		80.0	68.6	73.5	75.8	77.3	78.6	79.8	81.0	82.5	84.5	87.7	95.6
		90.0	78.6	83.5	85.8	87.3	88.6	89.8	91.0	92.5	94.5	97.7	105.6
		100.0	88.6	93.5	95.8	97.3	98.6	99.8	101.0	102.5	104.5	107.8	115.6
	10.0	10.0	6.3	7.8	8.5	9.0	9.3	9.7	10.2	10.9	11.8	13.4	17.2
		20.0	16.2	17.8	18.5	19.0	19.3	19.7	20.2	20.9	21.8	23.4	27.2
		30.0	26.2	27.8	28.5	29.0	29.3	29.7	30.2	30.9	31.8	33.4	37.2
		40.0	36.2	37.8	38.5	39.0	39.3	39.7	40.2	40.9	41.8	43.4	47.2
		50.0	46.2	47.8	48.5	49.0	49.3	49.7	50.2	50.9	51.8	53.4	57.2
		60.0	56.3	57.8	58.5	59.0	59.3	59.7	60.2	60.9	61.8	63.4	67.2
		70.0	66.2	67.8	68.5	69.0	69.3	69.7	70.2	70.9	71.8	73.4	77.2
		80.0	76.2	77.8	78.5	79.0	79.3	79.7	80.2	80.9	81.8	83.4	87.2
		90.0	86.2	87.8	88.5	89.0	89.3	89.7	90.2	90.9	91.8	93.4	97.2
		100.0	96.2	97.8	98.5	99.0	99.3	99.7	100.2	100.9	101.8	103.4	107.2

GENERALISED BREAKTHROUGH CURVES

CHARACTERISTIC TIME VALUES

MECHANISM PARAMETER	SEPARATION FACTOR	TRANSFER UNITS	X=0.0	0.0245	0.0955	0.2061	0.3455	0.5000	0.6545	0.7939	0.9045	0.9755	1.0000
0.5	0.1	10.0	0.0	0.0	0.0	0.0	0.7	2.3	5.3	12.0	29.2	76.3	180.0
		20.0	0.0	0.0	0.2	1.1	2.8	5.7	11.3	24.3	58.4	146.1	246.0
		30.0	0.0	0.0	0.9	2.4	4.8	9.0	17.4	36.7	87.6	210.6	281.0
		40.0	0.0	0.3	1.7	3.8	6.9	12.4	23.4	49.1	116.5	245.1	292.0
		50.0	0.0	0.7	2.6	5.2	9.0	15.8	29.4	61.2	145.1	281.1	328.0
		60.0	0.0	1.3	3.6	6.6	11.1	19.1	35.3	73.5	173.3	315.1	362.0
		70.0	0.0	2.0	4.6	8.0	13.2	22.4	41.3	85.9	203.0	345.1	392.0
		80.0	0.2	2.6	5.6	9.5	15.3	25.8	47.3	98.4	214.5	285.5	309.0
		90.0	0.3	3.3	6.9	10.9	17.5	29.1	53.2	110.6	259.0	401.1	448.0
		100.0	0.6	4.1	7.7	12.4	19.5	32.5	59.1	123.0	285.0	427.1	474.0
	0.5	10.0	0.0	0.0	1.5	3.0	5.0	7.6	11.1	15.8	22.5	32.4	52.5
		20.0	0.3	2.7	5.4	8.3	11.8	16.4	22.3	30.2	40.7	55.3	82.0
		30.0	2.0	6.0	9.8	13.7	18.9	25.2	33.5	44.4	58.4	77.3	109.0
		40.0	4.5	9.5	14.5	19.7	26.0	34.1	44.6	58.4	75.8	98.2	133.6
		50.0	6.5	13.4	19.3	25.6	33.2	42.9	55.7	72.4	93.1	119.2	159.0
		60.0	10.0	17.3	24.3	31.6	40.4	51.8	66.9	86.3	110.1	139.7	184.1
		70.0	12.0	21.6	29.3	37.5	47.7	60.7	77.9	100.2	127.2	160.3	200.0
		80.0	16.0	25.7	34.4	43.5	54.9	69.6	89.1	114.9	144.2	180.5	214.0
		90.0	20.0	30.1	39.5	49.6	62.1	78.5	100.1	127.7	161.1	200.5	224.0
		100.0	23.0	34.4	44.7	55.7	69.4	87.3	111.2	141.7	178.2	218.4	234.0
	0.8	10.0	0.0	1.1	2.8	4.6	6.5	8.8	11.5	14.8	19.0	25.4	39.0
		20.0	1.7	5.4	8.7	11.8	15.1	18.6	22.7	27.5	33.4	41.9	59.5
		30.0	5.0	10.7	15.3	19.5	23.8	28.4	33.7	39.7	47.1	57.5	77.1
		40.0	9.5	16.6	22.2	27.4	32.6	38.3	44.6	51.8	60.5	72.5	94.1
		50.0	14.0	22.8	29.4	35.4	41.5	48.1	55.4	63.7	73.7	87.2	111.0
		60.0	18.8	29.1	36.7	43.5	50.4	57.9	66.2	75.6	86.7	101.4	127.6
		70.0	24.7	35.5	44.1	51.7	59.4	67.8	77.0	87.3	99.5	115.7	142.7
		80.0	30.0	42.3	51.6	59.9	68.4	77.6	87.7	99.1	112.3	129.5	159.1
		90.0	35.2	48.9	59.2	68.2	77.5	87.5	98.5	110.8	124.9	143.3	174.1
		100.0	41.2	55.9	66.7	76.5	86.5	97.4	109.2	122.4	137.6	157.3	189.1
	1.0	10.0	0.0	1.6	3.5	5.3	7.2	9.2	11.5	14.1	17.6	22.8	34.0
		20.0	2.7	7.1	10.5	13.5	16.3	19.2	22.4	26.0	30.6	37.2	51.5
		30.0	7.6	13.6	18.2	22.0	25.6	29.2	33.1	37.5	42.8	50.7	67.0
		40.0	12.5	20.7	26.3	30.8	35.0	39.2	43.7	48.7	54.8	63.6	81.1
		50.0	18.5	28.2	34.6	39.7	44.5	49.2	54.2	59.8	66.5	76.2	95.1
		60.0	25.2	35.9	43.0	48.8	54.0	59.2	64.7	70.7	78.0	88.5	109.1
		70.0	32.2	43.7	51.6	57.9	63.6	69.2	75.1	81.6	89.5	100.6	122.1
		80.0	39.2	51.7	60.4	67.1	73.2	79.2	85.5	92.4	100.7	112.5	135.1
		90.0	46.2	59.9	69.1	76.3	82.9	89.2	95.9	103.2	111.9	124.5	148.0
		100.0	53.2	68.1	78.0	85.6	92.5	99.2	106.2	113.9	123.2	136.3	160.7
	1.2	10.0	0.0	2.2	4.2	5.9	7.7	9.5	11.4	13.6	16.6	21.1	31.0
		20.0	3.8	8.6	12.0	14.7	17.1	19.5	22.1	25.0	28.6	34.1	46.0
		30.0	9.6	16.2	20.5	23.8	26.8	29.6	32.5	35.9	40.0	46.2	60.0
		40.0	16.6	24.3	29.4	33.2	36.5	39.6	42.9	46.5	51.0	57.9	72.5
		50.0	23.5	32.8	38.5	42.7	46.3	49.7	53.1	57.0	61.9	69.3	84.1
		60.0	31.3	41.6	47.8	52.3	56.1	59.7	63.4	67.5	72.6	80.4	96.1
		70.0	39.2	50.4	57.2	61.9	65.9	69.7	73.6	77.8	83.2	91.4	108.1
		80.0	47.2	59.5	66.7	71.6	75.8	79.7	83.7	88.1	93.7	102.1	119.1
		90.0	56.1	68.7	76.2	81.4	85.7	89.7	93.8	98.4	104.2	112.9	131.1
		100.0	64.2	78.1	85.8	91.1	95.6	99.7	104.0	108.7	114.6	123.6	142.1
	2.0	10.0	1.0	4.0	5.9	7.4	8.6	9.8	11.0	12.4	14.3	17.4	24.6
		20.0	8.1	12.8	15.4	17.1	18.5	19.8	21.2	22.8	24.8	28.3	36.1
		30.0	16.6	22.5	25.2	27.0	28.5	29.8	31.2	32.9	35.0	38.4	46.6
		40.0	26.6	32.4	35.2	37.0	38.5	39.8	41.2	42.9	45.0	48.6	57.0
		50.0	36.1	42.3	45.2	47.0	48.5	49.8	51.2	52.9	55.1	58.6	67.0
		60.0	46.1	52.3	55.2	57.0	58.4	59.8	61.2	62.9	65.1	68.6	77.0
		70.0	56.1	62.3	65.1	67.0	68.4	69.8	71.3	72.9	75.1	78.6	87.0
		80.0	66.1	72.3	75.1	77.0	78.4	79.8	81.3	82.9	85.1	88.6	97.0
		90.0	76.1	82.3	85.1	87.0	88.4	89.8	91.3	92.9	95.1	98.6	107.0
		100.0	86.1	92.3	95.1	97.0	98.4	99.8	101.3	102.9	105.1	108.6	117.0
	10.0	10.0	5.0	7.3	8.3	8.9	9.3	9.8	10.3	11.0	12.0	13.6	17.6
		20.0	15.0	17.3	18.3	18.9	19.3	19.8	20.3	21.0	22.0	23.6	27.6
		30.0	25.0	27.3	28.3	28.9	29.3	29.8	30.3	31.0	32.0	33.6	37.6
		40.0	35.0	37.3	38.3	38.9	39.3	39.8	40.3	41.0	42.0	43.6	47.6
		50.0	45.0	47.3	48.3	48.9	49.3	49.8	50.3	51.0	52.0	53.6	57.6
		60.0	55.0	57.3	58.3	58.9	59.3	59.8	60.3	61.0	62.0	63.6	67.6
		70.0	65.0	67.3	68.3	68.9	69.3	69.8	70.3	71.0	72.0	73.6	77.6
		80.0	75.0	77.3	78.3	78.9	79.3	79.8	80.3	81.0	82.0	83.6	87.6
		90.0	85.0	87.3	88.3	88.9	89.3	89.8	90.3	91.0	92.0	93.6	97.6
		100.0	95.0	97.3	98.3	98.9	99.3	99.8	100.3	101.0	102.0	103.6	107.6

GENERALISED BREAKTHROUGH CURVES

CHARACTERISTIC TIME VALUES

MECHANISM PARAMETER	SEPARATION FACTOR	TRANSFER UNITS	X=0.0	0.0245	0.0955	0.2061	0.3455	0.5000	0.6545	0.7939	0.9045	0.9755	1.0000
1.0	0.1	10.0	0.0	0.0	0.0	0.0	0.4	2.0	4.8	11.3	28.5	79.1	192.1
		20.0	0.0	0.0	0.1	0.9	2.5	5.3	10.8	23.5	57.2	148.9	258.5
		30.0	0.0	0.0	0.7	2.2	4.5	8.6	16.8	35.7	86.3	213.6	284.0
		40.0	0.0	0.2	1.5	3.5	6.6	12.0	22.8	48.0	114.3	270.6	341.0
		50.0	0.0	0.6	2.5	4.9	8.7	15.3	28.7	60.4	143.3	279.1	326.0
		60.0	0.0	1.1	3.4	6.3	10.8	18.6	34.7	72.4	173.1	313.1	360.0
		70.0	0.0	1.8	4.3	7.7	12.9	21.9	40.6	84.9	201.0	343.1	390.0
		80.0	0.1	2.4	5.3	9.1	14.9	25.3	46.6	97.3	231.0	373.1	420.0
		90.0	0.2	3.0	6.4	10.6	17.0	28.6	52.5	109.3	257.0	399.1	446.0
		100.0	0.4	3.8	7.4	12.0	19.1	31.9	58.5	121.9	283.0	425.1	472.0
	0.5	10.0	0.0	0.0	1.0	2.5	4.4	7.1	10.8	16.0	23.5	35.8	61.0
		20.0	0.0	2.0	4.6	7.5	11.1	15.8	22.0	30.5	42.3	59.8	94.0
		30.0	1.5	4.9	8.8	13.0	18.1	24.5	33.2	44.8	60.3	82.2	121.5
		40.0	3.0	8.3	13.4	18.6	25.1	33.3	44.3	58.9	77.9	103.9	150.0
		50.0	6.0	12.1	18.0	24.4	32.2	42.2	55.4	72.9	95.3	125.7	176.1
		60.0	8.0	15.9	22.9	30.3	39.3	51.0	66.5	86.9	112.7	146.5	198.1
		70.0	10.0	19.9	27.8	36.2	46.5	59.9	77.7	100.8	129.8	167.5	206.0
		80.0	14.0	23.9	32.8	42.2	53.7	68.8	88.7	114.6	147.0	188.5	228.0
		90.0	17.0	28.1	37.8	48.2	60.9	77.6	99.8	128.4	164.2	205.7	221.3
		100.0	20.0	32.4	42.9	54.2	68.2	86.4	110.8	142.3	181.3	223.7	239.3
	0.8	10.0	0.0	0.0	2.0	3.9	6.0	8.5	11.5	15.2	20.2	27.9	45.0
		20.0	1.0	4.2	7.5	10.8	14.3	18.2	22.8	28.2	35.1	45.5	66.1
		30.0	3.5	9.1	13.8	18.3	22.9	28.0	33.8	40.7	49.3	61.4	86.0
		40.0	7.0	14.5	20.5	26.0	31.6	37.8	44.8	52.9	62.9	77.1	104.0
		50.0	11.2	20.3	27.4	33.8	40.5	47.6	55.7	65.0	76.3	92.0	121.6
		60.0	15.7	26.4	34.5	41.8	49.3	57.4	66.5	77.0	89.6	106.8	138.1
		70.0	20.2	32.6	41.7	49.9	58.2	67.3	77.4	88.9	102.6	121.3	154.6
		80.0	26.2	39.1	49.1	58.0	67.2	77.1	88.1	100.7	115.6	135.8	171.1
		90.0	31.0	45.6	56.4	66.2	76.2	87.0	98.9	112.5	128.5	149.7	186.2
		100.0	36.7	52.1	63.9	74.4	85.2	96.8	109.7	124.2	141.3	163.9	198.7
	1.0	10.0	0.0	0.8	2.7	4.6	6.7	9.0	11.6	14.7	18.8	25.1	39.5
		20.0	1.3	5.5	9.2	12.4	15.6	19.0	22.6	26.9	32.3	40.4	58.0
		30.0	5.0	11.5	16.5	20.7	24.8	29.0	33.5	38.6	45.0	54.3	73.1
		40.0	9.5	18.2	24.3	29.4	34.1	39.0	44.2	50.0	57.1	67.6	89.0
		50.0	15.2	25.3	32.3	38.1	43.6	49.0	54.7	61.2	69.1	80.6	104.0
		60.0	21.2	32.5	40.5	47.0	53.0	59.0	65.3	72.3	80.9	93.1	118.0
		70.0	27.2	40.1	49.0	56.0	62.5	69.0	75.8	83.4	92.5	105.8	132.0
		80.0	33.7	47.9	57.4	65.0	72.1	79.0	86.3	94.3	104.0	117.9	144.2
		90.0	40.9	55.6	66.0	74.2	81.6	89.0	96.7	105.2	115.4	130.3	157.7
		100.0	47.2	63.6	74.6	83.3	91.2	99.0	107.1	116.0	126.8	142.3	171.1
	1.2	10.0	0.0	1.2	3.2	5.2	7.2	9.3	11.6	14.3	17.7	23.1	35.5
		20.0	2.0	6.8	10.6	13.6	16.5	19.4	22.4	25.9	30.2	36.9	51.5
		30.0	6.6	13.7	18.7	22.6	26.1	29.5	33.0	37.0	41.9	49.4	66.0
		40.0	12.5	21.4	27.3	31.8	35.7	39.5	43.5	47.8	53.2	61.4	79.1
		50.0	19.2	29.4	36.2	41.1	45.5	49.6	53.8	58.5	64.3	73.1	91.1
		60.0	26.2	37.7	45.2	50.6	55.2	59.6	64.1	69.1	75.3	84.6	104.1
		70.0	33.2	46.3	54.3	60.1	65.0	69.6	74.3	79.6	86.0	95.9	116.1
		80.0	41.1	55.1	63.7	69.7	74.9	79.7	84.6	90.0	96.7	106.9	128.1
		90.0	49.1	64.1	73.0	79.4	84.7	89.7	94.8	100.4	107.3	117.9	140.0
		100.0	57.1	73.1	82.4	89.1	94.6	99.7	104.9	110.7	117.9	128.8	151.1
	2.0	10.0	0.0	2.5	4.8	6.7	8.3	9.8	11.3	13.1	15.3	19.0	27.1
		20.0	4.6	10.5	14.0	16.3	18.2	19.9	21.6	23.6	26.1	30.1	39.0
		30.0	12.6	19.8	23.6	26.2	28.2	29.9	31.8	33.8	36.3	40.4	50.0
		40.0	21.5	29.4	33.5	36.1	38.1	40.0	41.8	43.9	46.5	50.7	60.5
		50.0	30.5	39.3	43.4	46.1	48.1	50.0	51.8	53.9	56.5	60.8	71.0
		60.0	40.5	49.2	53.4	56.1	58.1	60.0	61.8	63.9	66.6	70.8	81.0
		70.0	50.5	59.2	63.4	66.1	68.1	70.0	71.8	73.9	76.6	80.9	91.0
		80.0	60.0	69.1	73.4	76.1	78.1	80.0	81.8	83.9	86.6	90.9	101.0
		90.0	70.0	79.1	83.4	86.1	88.1	90.0	91.8	93.9	96.6	100.9	111.0
		100.0	80.0	89.1	93.4	96.1	98.1	100.0	101.8	103.9	106.6	110.9	121.0
	10.0	10.0	2.1	5.9	7.6	8.6	9.4	10.0	10.6	11.3	12.4	14.1	18.2
		20.0	11.7	15.9	17.6	18.6	19.4	20.0	20.6	21.3	22.4	24.1	28.2
		30.0	21.7	25.9	27.6	28.6	29.4	30.0	30.6	31.3	32.4	34.1	38.2
		40.0	31.7	35.9	37.6	38.6	39.4	40.0	40.6	41.3	42.4	44.1	48.2
		50.0	41.7	45.9	47.6	48.6	49.4	50.0	50.6	51.3	52.4	54.1	58.2
		60.0	51.7	55.9	57.6	58.6	59.4	60.0	60.6	61.3	62.4	64.1	68.2
		70.0	61.7	65.9	67.6	68.6	69.4	70.0	70.6	71.3	72.4	74.1	78.2
		80.0	71.7	75.9	77.6	78.6	79.4	80.0	80.6	81.3	82.4	84.1	88.2
		90.0	81.7	85.9	87.6	88.6	89.4	90.0	90.6	91.3	92.4	94.1	98.2
		100.0	91.7	95.9	97.6	98.6	99.4	100.0	100.6	101.3	102.4	104.1	108.2

GENERALISED BREAKTHROUGH CURVES

CHARACTERISTIC TIME VALUES

MECHANISM PARAMETER	SEPARATION FACTOR	TRANSFER UNITS	X=0.0	0.0245	0.0955	0.2061	0.3455	0.5000	0.6545	0.7939	0.9045	0.9755	1.0000
2.0	0.1	10.0	0.0	0.0	0.0	0.1	0.9	2.3	4.9	11.0	27.8	77.3	196.0
		20.0	0.0	0.0	0.5	1.5	3.0	5.6	10.8	23.1	56.3	146.9	228.0
		30.0	0.0	0.3	1.4	2.9	5.0	8.9	16.7	35.3	84.9	211.6	282.0
		40.0	0.0	0.8	2.4	4.3	7.1	12.2	22.6	47.4	113.3	267.6	338.0
		50.0	0.1	1.6	3.4	5.7	9.2	15.5	28.5	59.6	142.3	279.1	326.0
		60.0	0.2	2.4	4.5	7.2	11.3	18.8	34.4	71.9	171.0	311.1	358.0
		70.0	0.4	3.1	5.5	8.6	13.4	22.1	40.3	83.9	201.0	343.0	390.0
		80.0	1.0	4.0	6.6	10.1	15.5	25.4	46.3	96.4	229.0	371.0	418.0
		90.0	2.0	4.7	7.7	11.6	17.6	28.7	52.1	108.6	255.0	397.1	444.0
		100.0	2.3	5.5	8.8	13.0	19.7	32.0	58.1	121.0	281.0	423.1	470.0
	0.5	10.0	0.0	0.5	1.7	3.1	4.9	7.4	10.7	15.5	22.5	33.3	57.0
		20.0	1.0	3.2	5.7	8.4	11.7	16.1	21.9	29.8	40.8	56.8	87.0
		30.0	3.0	6.6	10.2	14.1	18.7	24.8	33.0	43.9	58.6	79.2	114.1
		40.0	5.0	10.4	15.0	19.9	25.8	33.6	44.0	57.8	75.9	100.2	141.0
		50.0	8.0	14.4	19.9	25.8	33.0	42.4	55.1	71.8	93.3	121.7	166.1
		60.0	12.0	18.5	24.9	31.7	40.2	51.3	66.2	85.6	110.4	142.3	192.1
		70.0	14.0	22.7	30.0	37.7	47.4	60.1	77.1	99.6	127.5	162.5	207.0
		80.0	18.0	27.1	35.1	43.7	54.5	68.9	88.2	113.3	144.5	183.5	220.0
		90.0	22.0	31.5	40.2	49.8	61.8	77.8	99.3	127.2	161.4	203.5	227.0
		100.0	26.0	35.9	45.4	55.8	69.0	86.7	110.3	140.9	178.3	219.7	235.3
	0.8	10.0	0.0	1.2	2.8	4.6	6.5	8.7	11.4	14.7	19.0	25.6	40.0
		20.0	2.0	5.6	8.8	11.8	15.0	18.5	22.5	27.4	33.5	42.4	60.5
		30.0	5.5	11.0	15.4	19.5	23.7	28.3	33.5	39.6	47.3	58.1	79.0
		40.0	10.0	16.9	22.4	27.4	32.5	38.1	44.4	51.7	60.6	73.2	96.1
		50.0	14.5	23.1	29.6	35.4	41.4	47.9	55.2	63.6	73.8	87.8	113.0
		60.0	19.5	29.6	36.9	43.5	50.3	57.7	66.0	75.5	86.8	102.2	129.2
		70.0	25.5	36.1	44.3	51.7	59.3	67.6	76.7	87.2	99.7	116.3	145.6
		80.0	30.7	42.8	51.8	59.9	68.3	77.4	87.5	99.0	112.4	130.3	160.7
		90.0	36.7	49.6	59.4	68.2	77.3	87.2	98.3	110.7	125.2	144.3	177.1
		100.0	42.7	56.4	67.0	76.5	86.4	97.1	109.0	122.3	137.9	158.3	192.1
	1.0	10.0	0.0	1.6	3.5	5.3	7.2	9.2	11.5	14.1	17.6	22.8	34.0
		20.0	2.7	7.1	10.5	13.5	16.3	19.2	22.4	26.0	30.6	37.2	51.5
		30.0	7.6	13.6	18.2	22.0	25.6	29.2	33.1	37.5	42.9	50.7	67.0
		40.0	12.5	20.7	26.3	30.8	35.0	39.2	43.7	48.7	54.8	63.6	81.1
		50.0	18.5	28.2	34.6	39.7	44.5	49.2	54.2	59.8	66.5	76.2	95.1
		60.0	25.2	35.9	43.0	48.8	54.0	59.2	64.7	70.7	78.0	88.5	109.1
		70.0	32.2	43.7	51.6	57.9	63.6	69.2	75.1	81.6	89.5	100.6	122.1
		80.0	39.2	51.7	60.4	67.1	73.2	79.2	85.5	92.4	100.7	112.5	135.1
		90.0	46.2	59.9	69.1	76.3	82.9	89.2	95.9	103.2	111.9	124.5	148.0
		100.0	53.2	68.1	78.0	85.6	92.5	99.2	106.2	113.9	123.2	136.3	160.7
	1.2	10.0	0.0	2.1	4.1	5.9	7.7	9.5	11.5	13.7	16.5	20.8	30.5
		20.0	3.6	8.4	11.9	14.7	17.2	19.6	22.2	25.0	28.5	33.9	45.5
		30.0	9.1	15.9	20.4	23.8	26.8	29.7	32.6	35.9	39.9	45.9	59.0
		40.0	16.0	23.9	29.3	33.2	36.6	39.8	43.0	46.6	51.0	57.6	71.5
		50.0	22.5	32.4	38.4	42.7	46.4	49.8	53.3	57.1	61.8	68.9	83.1
		60.0	30.2	41.1	47.6	52.3	56.2	59.8	63.5	67.5	72.4	79.9	95.1
		70.0	38.2	50.1	57.0	61.9	66.1	69.9	73.7	77.9	83.1	90.9	107.1
		80.0	46.2	59.1	66.5	71.6	75.9	79.9	83.8	88.2	93.5	101.7	118.1
		90.0	55.1	68.3	76.0	81.4	85.8	89.9	94.0	98.5	104.0	112.4	129.1
		100.0	63.2	77.5	85.6	91.2	95.8	99.9	104.1	108.7	114.4	123.1	140.1
	2.0	10.0	0.5	3.4	5.7	7.4	8.7	10.0	11.2	12.5	14.2	16.7	22.6
		20.0	6.6	12.1	15.2	17.2	18.7	20.1	21.4	22.8	24.6	27.5	33.6
		30.0	15.1	21.7	25.0	27.1	28.7	30.1	31.5	32.9	34.8	37.7	44.1
		40.0	24.5	31.5	35.0	37.1	38.7	40.1	41.5	43.0	44.8	47.7	54.1
		50.0	34.0	41.4	44.9	47.1	48.7	50.1	51.5	53.0	54.8	57.8	64.6
		60.0	44.0	51.4	54.9	57.1	58.7	60.1	61.5	63.0	64.8	67.8	74.6
		70.0	54.0	61.4	64.9	67.1	68.7	70.1	71.5	73.0	74.8	77.8	84.6
		80.0	64.0	71.3	74.9	77.1	78.7	80.1	81.5	83.0	84.8	87.8	94.6
		90.0	74.0	81.3	84.9	87.1	88.7	90.1	91.5	93.0	94.8	97.8	104.6
		100.0	84.0	91.3	94.9	97.1	98.7	100.1	101.5	103.0	104.8	107.8	114.6
	10.0	10.0	2.6	6.4	8.0	9.0	9.6	10.1	10.6	11.0	11.6	12.7	15.0
		20.0	12.6	16.4	18.0	19.0	19.6	20.1	20.6	21.0	21.6	22.7	25.0
		30.0	22.6	26.4	28.0	29.0	29.6	30.1	30.6	31.0	31.6	32.7	35.0
		40.0	32.6	36.4	38.0	39.0	39.6	40.1	40.6	41.0	41.6	42.7	45.0
		50.0	42.6	46.4	48.0	49.0	49.6	50.1	50.6	51.0	51.6	52.7	55.0
		60.0	52.6	56.4	58.0	59.0	59.6	60.1	60.6	61.0	61.6	62.7	65.0
		70.0	62.6	66.4	68.0	69.0	69.6	70.1	70.6	71.0	71.6	72.7	75.0
		80.0	72.6	75.4	78.0	79.0	79.6	80.1	80.6	81.0	81.6	82.7	85.0
		90.0	82.6	86.4	88.0	89.0	89.6	90.1	90.6	91.0	91.6	92.7	95.0
		100.0	92.6	96.4	98.0	99.0	99.6	100.1	100.6	101.0	101.6	102.7	105.0

GENERALISED BREAKTHROUGH CURVES

CHARACTERISTIC TIME VALUES

MECHANISM PARAMETER	SEPARATION FACTOR	TRANSFER UNITS	X=0.0	0.0245	0.0955	0.2061	0.3455	0.5000	0.6545	0.7939	0.9045	0.9755	1.0000
3.0	0.1	10.0	0.0	0.0	-0.0	0.2	1.0	2.3	4.9	10.9	27.5	77.1	196.0
		20.0	0.0	0.1	0.7	1.8	3.1	5.7	10.8	22.9	56.2	146.6	233.0
		30.0	0.0	0.5	1.8	3.1	5.2	8.9	16.6	35.1	84.5	211.6	282.0
		40.0	0.1	1.2	2.8	4.6	7.3	12.2	22.6	47.3	113.5	243.1	290.0
		50.0	0.1	2.2	3.9	6.0	9.4	15.6	28.4	59.6	142.3	279.1	326.0
		60.0	0.4	2.8	4.9	7.5	11.5	18.8	34.4	71.5	171.0	311.1	358.0
		70.0	1.0	3.8	6.1	9.0	13.6	22.2	40.3	83.9	199.0	341.1	388.0
		80.0	2.0	4.6	7.1	10.4	15.7	25.5	46.1	95.9	229.0	371.0	418.0
		90.0	2.4	5.4	8.3	11.9	17.8	28.7	52.1	107.9	255.0	397.1	444.0
		100.0	3.0	6.3	9.4	13.4	19.9	32.0	57.9	120.5	281.0	423.1	470.0
	0.5	10.0	0.0	0.8	2.0	3.4	5.1	7.5	10.7	15.3	22.1	32.6	55.0
		20.0	0.9	3.8	6.2	8.8	11.9	16.1	21.8	29.6	40.2	55.8	85.0
		30.0	3.1	7.4	10.8	14.5	19.0	24.9	32.8	43.6	57.9	77.8	112.5
		40.0	6.0	11.2	15.6	20.3	26.1	33.7	43.9	57.5	75.3	99.2	138.0
		50.0	10.0	15.4	20.6	26.2	33.2	42.5	54.9	71.4	92.5	120.4	164.1
		60.0	12.0	19.5	25.7	32.2	40.4	51.3	65.9	85.3	109.6	140.6	188.1
		70.0	16.0	23.9	30.8	38.3	47.6	60.2	77.0	99.0	126.5	161.6	203.5
		80.0	20.0	28.4	36.0	44.3	54.9	69.0	88.1	112.9	143.5	181.5	218.0
		90.0	24.0	32.9	41.2	50.4	62.1	77.9	99.1	126.7	160.6	201.0	216.7
		100.0	28.0	37.3	46.4	56.5	69.3	86.7	110.1	140.4	177.3	218.4	234.0
	0.8	10.0	0.0	1.5	3.2	4.9	6.7	8.8	11.4	14.5	18.6	24.9	38.0
		20.0	2.5	6.2	9.3	12.2	15.2	18.6	22.4	27.0	32.9	41.4	58.5
		30.0	6.0	11.8	16.1	19.9	24.0	28.4	33.4	39.3	46.5	56.9	76.1
		40.0	11.0	17.8	23.1	27.9	32.8	38.1	44.2	51.2	59.7	71.6	93.1
		50.0	16.0	24.2	30.4	36.0	41.7	48.0	55.0	63.1	72.8	86.1	110.0
		60.0	21.5	30.8	37.8	44.1	50.7	57.8	65.8	74.9	85.8	100.4	126.0
		70.0	27.0	37.4	45.3	52.3	59.7	67.6	76.5	86.6	98.6	114.5	141.2
		80.0	33.0	44.3	52.9	60.6	68.7	77.5	87.3	98.3	111.3	128.4	157.6
		90.0	38.2	51.1	60.5	68.9	77.7	87.3	98.0	110.0	123.9	142.3	172.6
		100.0	44.2	58.1	68.2	77.3	86.8	97.2	108.7	121.6	136.6	155.7	187.6
	1.0	10.0	0.0	2.0	3.8	5.6	7.4	9.3	11.4	13.9	17.1	21.9	32.5
		20.0	3.2	7.7	11.0	13.8	16.5	19.3	22.3	25.7	30.0	36.3	49.0
		30.0	8.2	14.4	18.9	22.5	25.9	29.3	33.0	37.1	42.1	49.4	64.5
		40.0	14.0	21.7	27.0	31.3	35.3	39.3	43.5	48.2	53.9	62.1	78.1
		50.0	20.5	29.3	35.4	40.3	44.8	49.3	54.0	59.2	65.5	74.6	92.1
		60.0	27.2	37.1	44.0	49.4	54.4	59.3	64.4	70.1	77.0	86.9	105.1
		70.0	34.2	45.1	52.6	58.6	64.0	69.3	74.8	80.9	88.3	98.9	118.1
		80.0	41.2	53.3	61.4	67.8	73.6	79.3	85.2	91.7	99.6	110.6	131.1
		90.0	48.2	61.5	70.3	77.1	83.3	89.3	95.6	102.5	110.8	122.5	144.1
		100.0	56.3	69.9	79.1	86.4	92.9	99.3	105.9	113.1	121.8	134.2	157.0
	1.2	10.0	0.0	2.4	4.4	6.2	7.9	9.6	11.4	13.5	16.0	19.9	28.5
		20.0	4.2	9.0	12.4	15.1	17.4	19.7	22.1	24.7	27.9	32.8	43.0
		30.0	10.1	16.7	21.1	24.3	27.1	29.8	32.5	35.5	39.1	44.6	56.5
		40.0	17.1	24.9	30.0	33.7	36.9	39.8	42.8	46.1	50.1	56.1	69.0
		50.0	24.5	33.5	39.2	43.3	46.7	49.9	53.1	56.6	60.9	67.2	81.0
		60.0	32.2	42.4	48.6	52.9	56.6	59.9	63.3	66.9	71.4	78.3	92.1
		70.0	40.2	51.4	58.0	62.6	66.4	69.9	73.4	77.3	82.0	89.1	103.2
		80.0	48.2	60.5	67.5	72.3	76.3	80.0	83.6	87.5	92.5	99.9	114.2
		90.0	57.2	69.9	77.1	82.1	86.2	90.0	93.7	97.8	102.8	110.4	126.1
		100.0	66.1	79.1	86.8	91.9	96.1	100.0	103.8	108.0	113.2	120.9	137.1
	2.0	10.0	0.5	3.8	6.0	7.6	8.9	10.1	11.1	12.3	13.8	16.0	21.1
		20.0	7.1	12.6	15.6	17.5	18.9	20.1	21.3	22.6	24.1	26.5	31.6
		30.0	16.1	22.4	25.5	27.4	28.9	30.2	31.4	32.6	34.2	36.7	42.1
		40.0	25.5	32.2	35.4	37.4	38.9	40.2	41.4	42.7	44.3	46.7	52.1
		50.0	35.1	42.2	45.4	47.4	48.9	50.2	51.4	52.7	54.2	56.7	62.1
		60.0	45.1	52.2	55.4	57.4	58.9	60.2	61.4	62.7	64.3	66.7	72.1
		70.0	55.1	62.2	65.4	67.4	68.9	70.2	71.4	72.7	74.3	76.7	82.1
		80.0	65.1	72.1	75.4	77.4	78.9	80.2	81.4	82.7	84.3	86.7	92.1
		90.0	75.0	82.1	85.4	87.4	88.9	90.2	91.4	92.7	94.3	96.7	102.1
		100.0	85.0	92.1	95.4	97.4	98.9	100.2	101.4	102.7	104.3	106.7	112.1
	10.0	10.0	3.2	6.6	8.2	9.1	9.7	10.2	10.6	11.0	11.5	12.2	13.8
		20.0	13.2	16.6	18.2	19.1	19.7	20.2	20.6	21.0	21.5	22.2	23.8
		30.0	23.2	26.6	28.2	29.1	29.7	30.2	30.6	31.0	31.5	32.2	33.8
		40.0	33.2	36.6	38.2	39.1	39.7	40.2	40.6	41.0	41.5	42.2	43.8
		50.0	43.2	46.6	48.2	49.1	49.7	50.2	50.6	51.0	51.5	52.2	53.8
		60.0	53.2	56.6	58.2	59.1	59.7	60.2	60.6	61.0	61.5	62.2	63.8
		70.0	63.2	66.6	68.2	69.1	69.7	70.2	70.6	71.0	71.5	72.2	73.8
		80.0	73.2	76.6	78.2	79.1	79.7	80.2	80.6	81.0	81.5	82.2	83.8
		90.0	83.2	86.6	88.2	89.1	89.7	90.2	90.6	91.0	91.5	92.2	93.8
		100.0	93.2	96.6	98.2	99.1	99.7	100.2	100.6	101.0	101.5	102.2	103.8

GENERALISED BREAKTHROUGH CURVES

CHARACTERISTIC TIME VALUES

MECHANISM PARAMETER	SEPARATION FACTOR	TRANSFER UNITS	X=0.0	0.0245	0.0955	0.2061	0.3455	0.5000	0.6545	0.7939	0.9045	0.9755	1.0000
10.0	0.1	10.0	0.0	-0.0	0.1	0.4	1.2	2.4	4.9	10.7	27.2	77.1	198.0
		20.0	0.0	0.3	1.1	2.1	3.4	5.8	10.7	22.7	55.7	145.6	258.5
		30.0	0.0	0.9	2.3	3.6	5.5	9.0	16.5	34.8	84.3	210.6	281.0
		40.0	0.2	2.2	3.4	5.0	7.5	12.3	22.4	46.8	112.3	243.1	290.0
		50.0	1.0	2.8	4.6	6.5	9.6	15.6	28.2	59.2	141.0	318.6	389.0
		60.0	2.1	4.0	5.7	8.0	11.7	18.9	34.1	71.1	170.3	311.1	358.0
		70.0	2.3	4.7	6.8	9.5	13.8	22.1	39.9	83.4	199.0	341.1	388.0
		80.0	4.0	5.8	8.0	11.0	15.9	25.4	45.9	95.4	227.0	369.1	416.0
		90.0	4.2	6.7	9.1	12.4	18.0	28.7	51.9	107.9	226.5	297.5	321.0
		100.0	4.7	7.6	10.3	13.9	20.1	32.0	57.6	119.9	279.0	421.1	468.0
	0.5	10.0	0.0	1.3	2.5	3.7	5.4	7.6	10.6	15.0	21.5	31.6	52.5
		20.0	2.0	4.6	6.9	9.3	12.3	16.2	21.7	29.1	39.4	54.3	82.0
		30.0	5.0	8.5	11.7	15.1	19.3	25.0	32.7	43.1	56.9	76.3	109.0
		40.0	8.0	12.6	16.7	21.0	26.4	33.7	43.7	57.0	74.3	97.3	135.0
		50.0	12.0	16.9	21.7	27.0	33.6	42.5	54.7	70.8	91.4	118.2	159.0
		60.0	14.7	21.3	26.9	33.0	40.8	51.4	65.7	84.5	108.4	138.3	184.1
		70.0	18.7	25.8	32.1	39.0	48.0	60.2	76.7	98.4	125.2	158.5	200.0
		80.0	22.0	30.4	37.3	45.1	55.3	69.1	87.6	112.2	142.2	178.9	214.0
		90.0	26.0	35.0	42.6	51.2	62.5	77.9	98.8	126.0	159.0	199.5	223.0
		100.0	30.0	39.6	48.0	57.3	69.8	86.7	109.7	139.7	175.8	216.4	232.0
	0.8	10.0	0.5	2.1	3.7	5.3	7.0	8.9	11.3	14.2	17.9	23.6	35.5
		20.0	3.5	7.2	10.1	12.8	15.6	18.7	22.3	26.6	32.0	39.7	55.0
		30.0	8.0	13.0	17.0	20.6	24.4	28.5	33.2	38.7	45.4	54.9	72.1
		40.0	13.0	19.3	24.2	28.7	33.2	38.3	43.9	50.5	58.6	69.5	89.1
		50.0	18.5	25.9	31.6	36.8	42.2	48.1	54.7	62.3	71.5	83.8	105.1
		60.0	24.0	32.6	39.2	45.1	51.2	57.9	65.4	74.1	84.3	97.8	121.1
		70.0	29.5	39.4	46.7	53.4	60.2	67.7	76.1	85.7	96.9	111.8	137.0
		80.0	36.0	46.4	54.4	61.7	69.3	77.5	86.8	97.3	109.6	125.4	151.7
		90.0	42.0	53.5	62.2	70.1	78.3	87.4	97.5	108.9	122.2	139.3	166.7
		100.0	48.7	60.5	70.0	78.5	87.4	97.2	108.2	120.5	134.6	152.8	181.7
	1.0	10.0	0.5	2.5	4.3	6.0	7.7	9.4	11.4	13.6	16.4	20.7	29.6
		20.0	4.2	8.6	11.8	14.4	16.9	19.4	22.1	25.2	29.0	34.6	46.0
		30.0	9.7	15.6	19.8	23.2	26.3	29.4	32.7	36.4	41.0	47.6	60.5
		40.0	16.1	23.2	28.2	32.2	35.8	39.4	43.2	47.5	52.6	60.1	74.5
		50.0	22.5	31.1	36.7	41.2	45.4	49.4	53.7	58.4	64.0	72.1	87.2
		60.0	29.5	39.1	45.4	50.4	55.0	59.4	64.1	69.2	75.4	84.1	100.1
		70.0	36.5	47.3	54.2	59.6	64.6	69.4	74.4	79.9	86.6	95.9	113.1
		80.0	44.2	55.5	63.1	69.0	74.3	79.4	84.8	90.6	97.7	107.6	126.1
		90.0	52.2	63.9	72.0	78.3	83.9	89.4	95.1	101.3	108.8	119.2	138.1
		100.0	59.2	72.5	81.0	87.7	93.6	99.4	105.4	111.9	119.8	130.8	151.1
	1.2	10.0	0.5	2.9	4.9	6.6	8.2	9.7	11.3	13.1	15.4	18.7	26.1
		20.0	5.2	10.0	13.2	15.6	17.8	19.8	21.9	24.2	27.0	31.2	40.0
		30.0	11.6	17.9	22.0	25.0	27.5	29.9	32.3	34.9	38.1	42.8	52.5
		40.0	19.1	26.4	31.2	34.5	37.3	39.9	42.5	45.4	48.8	53.9	64.5
		50.0	26.6	35.3	40.5	44.1	47.2	50.0	52.7	55.8	59.4	64.9	76.5
		60.0	35.0	44.2	49.9	53.8	57.1	60.0	62.9	66.1	69.9	75.8	87.5
		70.0	43.5	53.4	59.5	63.6	67.0	70.0	73.1	76.4	80.4	86.4	99.0
		80.0	52.0	62.7	69.1	73.4	76.9	80.1	83.2	86.6	90.7	96.9	110.0
		90.0	60.2	72.1	78.7	83.2	86.8	90.1	93.3	96.8	101.0	107.5	120.2
		100.0	69.2	81.7	88.5	93.1	96.8	100.1	103.4	106.9	111.3	117.9	131.2
	2.0	10.0	1.0	4.3	6.5	8.0	9.1	10.1	11.1	12.0	13.1	14.9	18.8
		20.0	8.1	13.5	16.2	17.9	19.2	20.2	21.2	22.2	23.4	25.2	29.2
		30.0	17.1	23.3	26.1	27.9	29.2	30.2	31.2	32.2	33.4	35.3	39.2
		40.0	27.1	33.2	36.1	37.9	39.2	40.2	41.2	42.2	43.5	45.3	49.2
		50.0	36.6	43.2	46.1	47.9	49.2	50.2	51.2	52.3	53.5	55.3	59.2
		60.0	46.6	53.1	56.1	57.9	59.2	60.2	61.2	62.3	63.5	65.3	69.2
		70.0	56.6	63.1	66.1	67.9	69.2	70.2	71.2	72.3	73.5	75.3	79.2
		80.0	66.6	73.1	76.1	77.9	79.2	80.2	81.2	82.3	83.5	85.3	89.2
		90.0	76.6	83.1	86.1	87.9	89.2	90.2	91.2	92.3	93.5	95.3	99.2
		100.0	86.6	93.1	96.1	97.9	99.2	100.2	101.2	102.3	103.5	105.3	109.2
	10.0	10.0	3.4	6.8	8.3	9.2	9.8	10.3	10.6	10.9	11.2	11.6	12.2
		20.0	13.4	16.8	18.3	19.2	19.8	20.3	20.6	20.9	21.2	21.6	22.2
		30.0	23.4	26.8	28.3	29.2	29.8	30.3	30.6	30.9	31.2	31.5	32.2
		40.0	33.4	36.8	38.3	39.2	39.8	40.2	40.6	40.9	41.2	41.5	42.2
		50.0	43.4	46.8	48.3	49.2	49.8	50.2	50.6	50.9	51.2	51.5	52.2
		60.0	53.4	56.7	58.3	59.2	59.8	60.2	60.6	60.9	61.1	61.5	62.2
		70.0	63.4	66.7	68.3	69.2	69.8	70.2	70.6	70.9	71.1	71.5	72.2
		80.0	73.2	76.7	78.3	79.1	79.8	80.2	80.6	80.9	81.1	81.5	82.2
		90.0	83.2	86.7	88.3	89.1	89.7	90.2	90.5	90.8	91.1	91.5	92.2
		100.0	93.2	96.7	98.2	99.1	99.7	100.2	100.5	100.8	101.1	101.5	102.2

GENERALISED BREAKTHROUGH CURVES

CHARACTERISTIC TIME VALUES

MECHANISM PARAMETER	SEPARATION FACTOR	TRANSFER UNITS	X=0.0	0.0245	0.0955	0.2061	0.3455	0.5000	0.6545	0.7939	0.9045	0.9755	1.0000
INFINITE	0.1	10.0	0.0	0.0	0.1	0.5	1.3	2.4	4.8	10.6	27.0	76.3	198.0
		20.0	0.0	0.4	1.4	2.3	3.5	5.8	10.6	22.6	55.2	144.9	258.5
		30.0	0.1	1.8	2.9	3.8	5.6	9.0	16.4	34.6	83.6	210.6	281.0
		40.0	0.7	2.5	3.9	5.2	7.6	12.3	22.2	46.6	112.5	243.1	290.0
		50.0	2.1	3.5	4.9	6.7	9.7	15.5	28.1	58.8	141.1	317.6	388.0
		60.0	2.3	4.5	6.2	8.2	11.8	18.8	33.9	70.9	169.3	311.1	358.0
		70.0	4.0	5.5	7.3	9.7	13.9	22.1	39.9	83.3	199.0	341.1	388.0
		80.0	4.2	6.5	8.5	11.2	16.0	25.4	45.7	95.3	227.0	369.1	416.0
		90.0	5.0	7.5	9.7	12.7	18.1	28.6	51.6	107.9	253.0	395.1	442.0
		100.0	6.2	8.5	10.8	14.2	20.2	32.0	57.6	119.9	279.0	421.1	468.0
	0.5	10.0	0.2	1.5	2.7	3.9	5.5	7.6	10.6	14.9	21.1	31.1	51.6
		20.0	2.3	5.0	7.2	9.5	12.4	16.3	21.6	28.9	39.1	53.8	81.0
		30.0	5.2	9.0	12.1	15.3	19.5	25.0	32.6	42.8	56.5	75.3	108.0
		40.0	8.4	13.2	17.1	21.3	26.6	33.8	43.6	56.7	73.7	96.3	133.0
		50.0	12.8	17.6	22.2	27.3	33.8	42.6	54.5	70.5	90.8	117.0	158.4
		60.0	16.2	22.1	27.4	33.4	41.0	51.4	65.6	84.2	107.9	137.3	183.7
		70.0	19.8	26.7	32.7	39.4	48.2	60.2	76.6	98.1	124.8	158.0	199.8
		80.0	23.4	31.3	38.0	45.5	55.5	69.1	87.6	111.8	141.7	177.8	210.6
		90.0	27.6	35.9	43.2	51.6	62.7	77.9	98.6	125.5	158.6	198.5	219.6
		100.0	32.4	40.6	48.6	57.8	70.0	86.7	109.5	139.3	175.3	213.9	228.0
	0.8	10.0	0.5	2.3	3.9	5.5	7.1	9.0	11.2	14.0	17.6	23.1	34.5
		20.0	4.0	7.6	10.4	13.0	15.7	18.7	22.2	26.3	31.5	39.1	53.5
		30.0	9.0	13.7	17.5	20.9	24.6	28.5	33.0	38.4	44.9	54.1	71.1
		40.0	14.0	20.1	24.8	29.0	33.5	38.3	43.8	50.2	58.0	68.5	87.1
		50.0	19.5	26.7	32.2	37.2	42.4	48.2	54.6	62.0	70.8	82.8	103.1
		60.0	25.5	33.5	39.8	45.5	51.4	58.0	65.3	73.6	83.6	96.8	119.1
		70.0	31.5	40.4	47.5	53.9	60.5	67.8	76.0	85.3	96.2	110.4	135.0
		80.0	37.5	47.6	55.2	62.2	69.5	77.6	86.6	96.9	108.8	124.3	148.9
		90.0	43.5	54.7	63.0	70.6	78.6	87.4	97.3	108.4	121.3	137.8	163.9
		100.0	50.2	61.8	70.8	79.0	87.7	97.3	108.0	120.0	133.7	151.3	178.7
	1.0	10.0	0.8	2.8	4.6	6.2	7.8	9.5	11.3	13.4	16.1	20.2	28.6
		20.0	4.7	9.1	12.2	14.7	17.1	19.5	22.1	25.0	28.6	33.9	44.5
		30.0	10.6	16.3	20.3	23.5	26.5	29.5	32.6	36.2	40.5	46.6	59.0
		40.0	17.1	23.9	28.7	32.5	36.0	39.5	43.1	47.1	52.0	59.1	72.5
		50.0	23.5	31.8	37.3	41.7	45.6	49.5	53.5	58.0	63.4	71.1	85.2
		60.0	30.5	39.9	46.1	50.9	55.2	59.5	63.9	68.8	74.7	82.9	98.1
		70.0	38.2	48.3	54.9	60.2	64.9	69.5	74.3	79.5	85.8	94.6	111.1
		80.0	45.5	56.7	63.8	69.5	74.6	79.5	84.6	90.2	96.9	106.3	123.1
		90.0	53.5	65.1	72.8	78.8	84.2	89.5	94.9	100.8	107.9	117.9	136.1
		100.0	61.2	73.7	81.9	88.3	93.9	99.5	105.2	111.4	118.9	129.2	148.1
	1.2	10.0	1.0	3.2	5.2	6.8	8.3	9.8	11.3	13.0	15.1	18.2	24.6
		20.0	5.7	10.5	13.5	15.9	17.9	19.9	21.8	24.0	26.6	30.4	38.6
		30.0	12.6	18.6	22.4	25.3	27.7	29.9	32.2	34.6	37.6	41.9	51.0
		40.0	20.1	27.2	31.7	34.9	37.5	40.0	42.4	45.1	48.3	53.1	63.0
		50.0	28.0	36.1	41.1	44.6	47.4	50.0	52.6	55.4	58.8	63.9	74.5
		60.0	36.1	45.2	50.6	54.3	57.3	60.1	62.8	65.7	69.3	74.6	85.5
		70.0	44.5	54.4	60.2	64.1	67.2	70.1	72.9	75.9	79.6	85.3	96.5
		80.0	53.5	63.7	69.8	73.9	77.2	80.1	83.0	86.1	89.9	95.8	107.5
		90.0	62.5	73.2	79.5	83.7	87.1	90.1	93.1	96.3	100.2	106.1	118.0
		100.0	71.5	82.7	89.3	93.6	97.1	100.2	103.2	106.4	110.4	116.4	129.0
	2.0	10.0	1.3	4.6	6.7	8.2	9.3	10.2	11.1	11.9	12.9	14.4	17.5
		20.0	8.6	13.9	16.5	18.1	19.3	20.3	21.2	22.0	23.1	24.6	27.7
		30.0	18.1	23.7	26.4	28.1	29.3	30.3	31.2	32.1	33.1	34.7	38.0
		40.0	27.6	33.6	36.4	38.1	39.3	40.3	41.2	42.1	43.1	44.7	48.0
		50.0	37.6	43.6	46.4	48.1	49.3	50.3	51.2	52.1	53.1	54.7	58.0
		60.0	47.6	53.6	56.4	58.1	59.3	60.3	61.2	62.1	63.1	64.7	68.0
		70.0	57.6	63.6	66.4	68.1	69.3	70.3	71.2	72.1	73.1	74.7	78.0
		80.0	67.6	73.6	76.4	78.1	79.3	80.3	81.2	82.1	83.1	84.7	88.0
		90.0	77.6	83.6	86.4	88.1	89.3	90.3	91.2	92.1	93.1	94.7	98.0
		100.0	87.6	93.6	96.4	98.1	99.3	100.3	101.2	102.1	103.1	104.7	108.0
	10.0	10.0	3.2	6.9	8.4	9.3	9.9	10.3	10.6	10.9	11.2	11.4	11.5
		20.0	13.2	16.8	18.4	19.2	19.8	20.3	20.6	20.8	21.2	21.4	21.5
		30.0	23.1	26.8	28.3	29.2	29.8	30.3	30.6	30.8	31.1	31.4	31.5
		40.0	33.1	36.8	38.3	39.2	39.8	40.2	40.6	40.8	41.1	41.4	41.5
		50.0	43.1	46.8	48.3	49.2	49.8	50.2	50.6	50.8	51.1	51.4	51.5
		60.0	53.1	56.8	58.3	59.2	59.8	60.2	60.6	60.8	61.1	61.4	61.5
		70.0	63.1	66.8	68.3	69.2	69.8	70.2	70.6	70.8	71.1	71.4	71.5
		80.0	73.1	76.8	78.3	79.2	79.8	80.2	80.6	80.8	81.1	81.4	81.5
		90.0	83.1	86.8	88.3	89.2	89.8	90.2	90.6	90.8	91.1	91.4	91.5
		100.0	93.1	96.8	98.3	99.2	99.8	100.2	100.6	100.8	101.1	101.4	101.5

CHAPTER 6

THE LINEAR PARTICLE DIFFUSION MODEL (AIXLR) - ANALOGUE SOLUTION

The equations of the model, IXLR, of the fixed-bed ion exchange process were solved in the previous chapter using digital computer methods. This chapter is concerned with the analogue computer solution of these same equations.

Both chapters produce equivalent results. Since the methods of solution are substantially different, both are thereby confirmed.

6-1 ANALOG FORMULATION OF EQUATIONS

An analogue computer is most effective when solving a set of ordinary differential equations. Table 5-1 lists the equations of the IXLR model which can be reduced to such a set if an appropriate finite difference representation is used for the differential $\frac{\partial x}{\partial N}$ in terms of a transfer unit increment ΔN:-

$$\frac{\partial x_i}{\partial N} = \frac{a \cdot x_{i+1} + b \cdot x_i + c \cdot x_{i-1}}{2\Delta N} \qquad (6\text{-}1)$$

Here, a, b and c are weights whose values depend on the particular finite difference approximation being used. The profile, x_i (T), is a breakthrough curve at a column depth $N = i \times \Delta N$, and is a function of T alone. The solution to the model equations will not be a surface above the N,T plane, but a series of curves in that surface spaced ΔN apart.

The equations to be solved are listed in Table 6-1. This set of equations must be solved for each profile required down the column to the number of transfer units required.

The analogue computer solves these equations starting at T = 0, in RESET (or initial condition mode), with initial conditions applied to the y integrators corresponding to the initial resin concentration at that depth in the column. When the computer is placed in OPERATE (the computing mode) all equations are dynamically solved at continuously increasing values of the independent variable, T, corresponding to increasing time.

Source	General Form	Analogue Form	
Solution mass balance, Eqn 6-1.	$\frac{\partial x}{\partial N} + \frac{\partial y}{\partial T} = 0$	$\frac{dy}{dT} = - \frac{a\ x_{i+1} + b\ x_i + c\ x_{i-1}}{2\Delta N}$	(6-2)
Particle rate, Eqn 2-7.	$\frac{\partial y}{\partial T} = \sigma(y^* - y)$	$y^* = y + \frac{1}{\sigma} \frac{dy}{dT}$	(6-3)
Surface equilibrium, Eqn 2-4.	$\frac{y^*}{1 - y^*} = K \frac{x^*}{1 - x^*}$	$x^* = \frac{y^*}{y^* + K(1 - y^*)}$	(6-4)
Solution rate, Eqn 2-8.	$\frac{\partial y}{\partial T} = \rho(x - x^*)$	$x_i = x^* + \frac{1}{\rho} \frac{dy}{dT}$	(6-5)

TABLE 6-1. Equations for the analogue computer model, AIXLR.

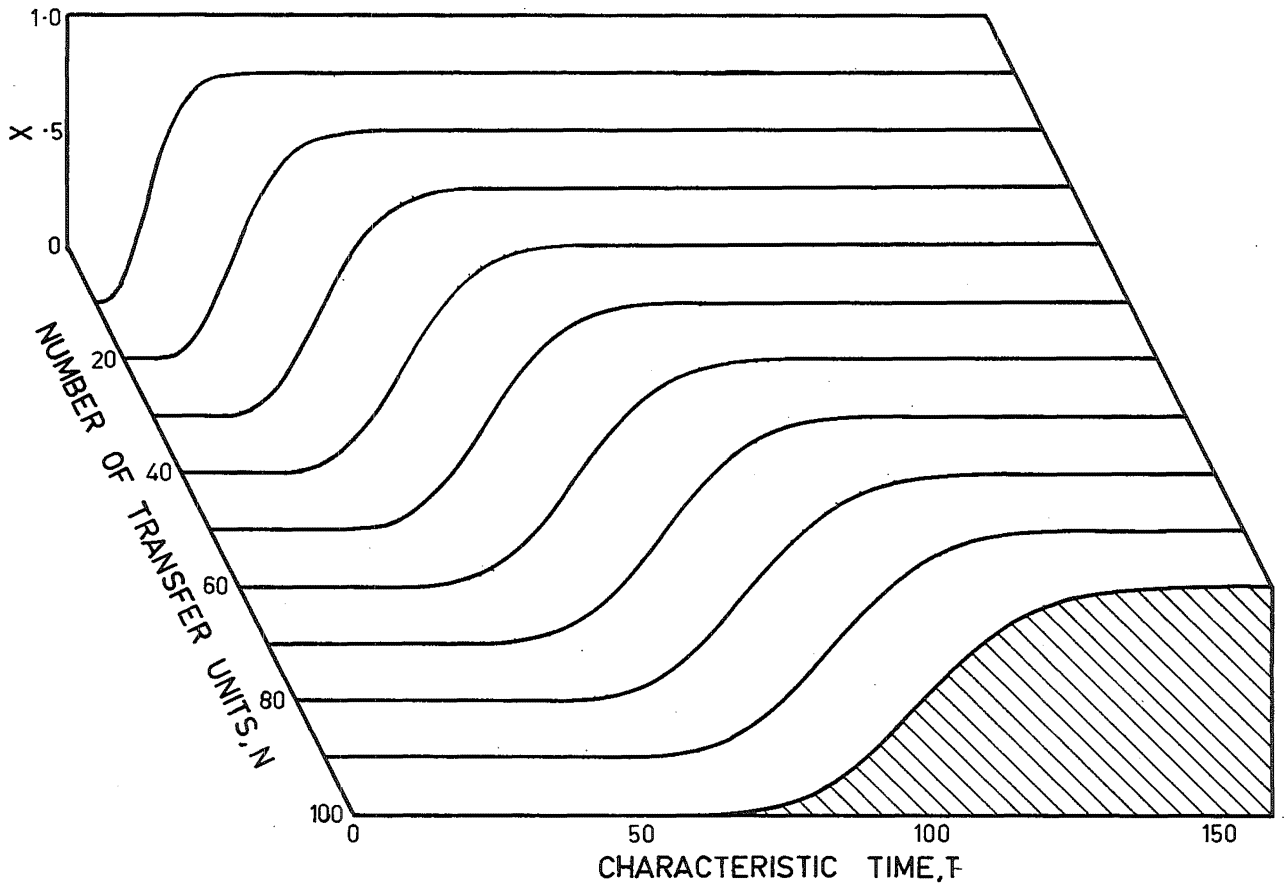


FIGURE 6-1. THE ANALOG COMPUTER SOLUTION AS A SERIES OF CURVES IN THE SOLUTION SURFACE.

The method of solving the equations for a single profile $x_i(T)$ is shown in Figure 6-2. The complete solution is built up from a number of such cells, all operating together.

This parallelism allows very fast computing speeds - a single solution for this problem on a typical analogue computer taking tens of milliseconds. If the results are to be retained, however, the analogue must be restrained to match the slower mechanical plotting device.

The disadvantage is that excessive computing equipment is required. For a column of 50 transfer units with a likely step-size $\Delta N = 2.0$, 25 repetitions of the equipment for a single cell are required.

6-2 The Tape-Recorder Solution

The method of this section is included as something of a curiosity rather than as a standard tool for the simulation of fixed-bed systems.

If a first-order finite difference approximation is used:-

$$\frac{dy_i}{dT} = - \frac{x_i - x_{i-1}}{\Delta N}$$

then only the present and previous profiles are required in a single cell. One cell could then be used successively, rather than many cells once, provided a profile could be stored and played back to calculate the next profile which could be stored in turn for next use.

A hybrid computer (Chapters 8, 9) is intended for this purpose, but may not be available. McGreavy (1967) mentions the use of an XY-plotter with a curve-follower. However, the device used in this thesis was a four-channel, frequency-modulated tape recorder, operating with a continuous loop of tape to store voltage signals.

The voltage level on one channel controlled the analogue computer mode, either in RESET or OPERATE. Two other channels were used to store profiles alternately, one playing back a previous solution and the other recording the present profile.

Some results (Graph 6-1) were obtained for a separation factor of 1.33 and particle phase control. Sufficient components on the avail-

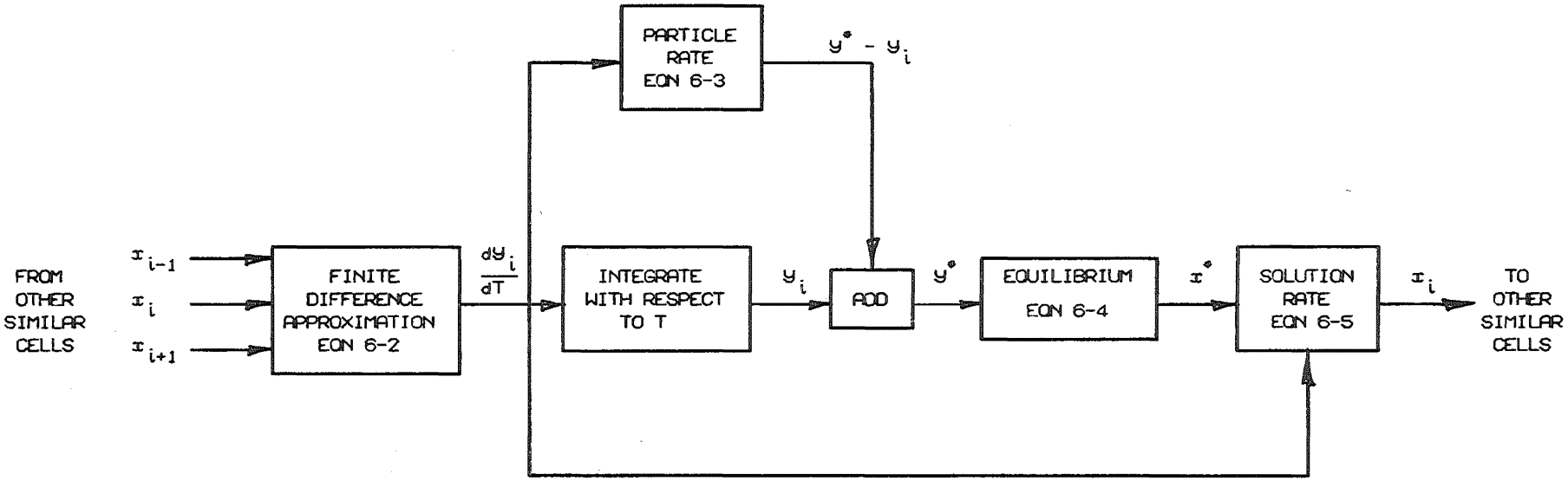


FIGURE 6-2. ANALOG CALCULATION OF A SINGLE PROFILE $x_i(T)$.

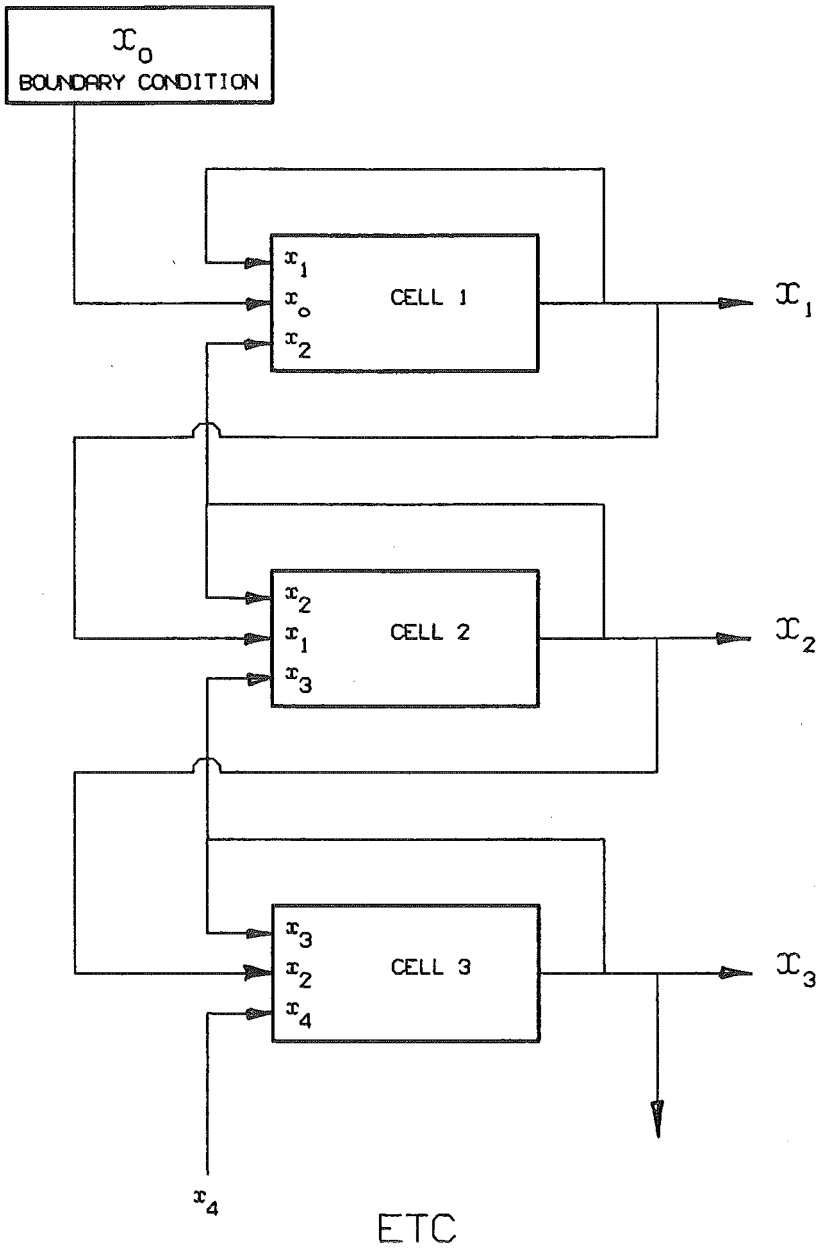
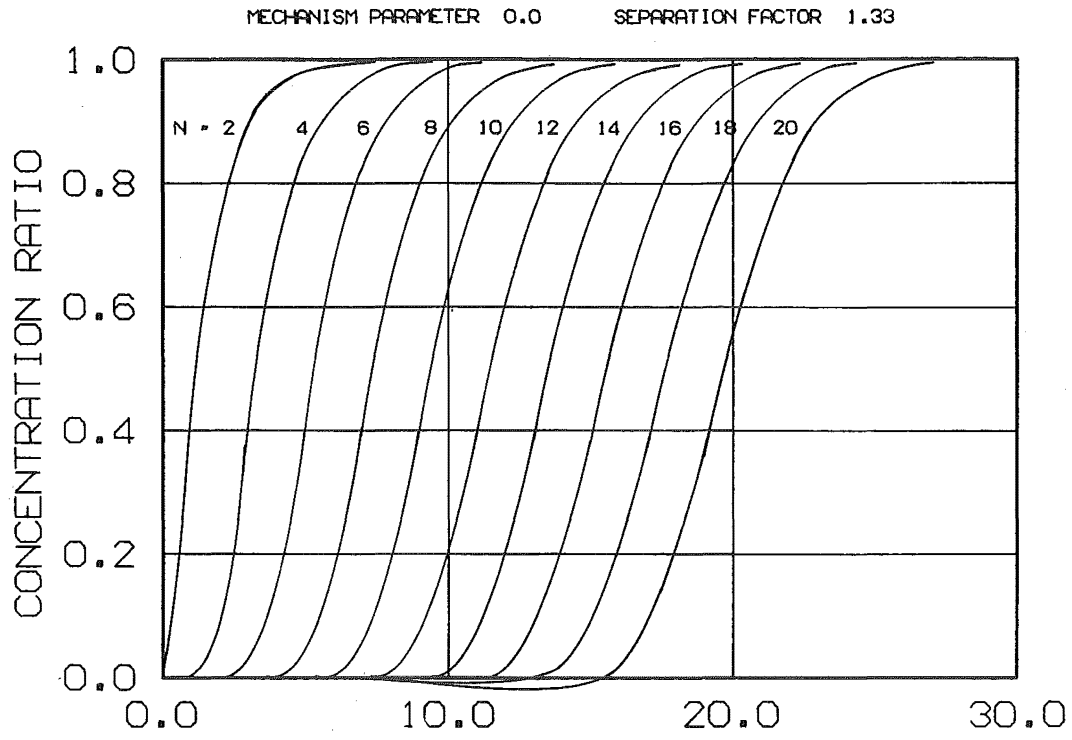


FIGURE 6-3. ARRANGEMENT OF COMPUTATIONAL CELLS FOR COMPLETE COLUMN SIMULATION.



GRAPH 6-1. BREAKTHROUGH CURVES-ANALOG COMPUTER WITH TAPE RECORDER STORAGE.

able 36 amplifier EAI TR-48 analogue computer allowed three cells to be patched. With a step-size of $\Delta N = \frac{2}{3}$ the solution proceeded by two transfer units per cycle of the tape.

The considerable electric noise on the tape had surprisingly little effect on the solution, probably because of integration in each cell. A more difficult problem was the zero drift in the tape recorder. This drift when integrated, caused the concentration ratio to fall below zero, and to fail to tend to 1.0.

6-3 The Parallel Analogue Computer Solution

The 105 amplifier EAI-8800 at the Division of Chemical Engineering, CSIRO, Melbourne, Victoria, was used to solve the ion exchange equations using the parallel method. Ten cells could be patched.

A second-order finite difference approximation was used:-

$$\frac{dx_i}{dN} = \frac{x_{i+1} - x_{i-1}}{2\Delta N} \quad \text{for all cells except the last}$$

$$\frac{dx_{10}}{dN} = \frac{3x_{10} - 4x_9 + x_8}{2\Delta N} \quad \text{for the last cell.}$$

The analogue circuit used is shown in Figure 6-4. The only section that requires comment is the equilibrium calculation of x*. The factor F was normally 2.0, but for a separation factor greater than 2.0, F was increased to 10.0. The patching modification required for unfavourable equilibrium is included to keep potentiometer values positive. A better method is discussed in Chapter 8.

The verification of this solution was similar to that of the digital computer solution. The J function is available for linear equilibrium. Equilibrium and rate calculations were verified by halting the computer and reading values for manual checking.

Step-sizes were in general selected so that the convergence error was less than 1%, reasonable in comparison with the accuracy of a single analogue computer component (0.01% to 0.5%) and the number of components in use. Several step sizes were used for almost every set of conditions computed.

Typical step-sizes for the required accuracy were

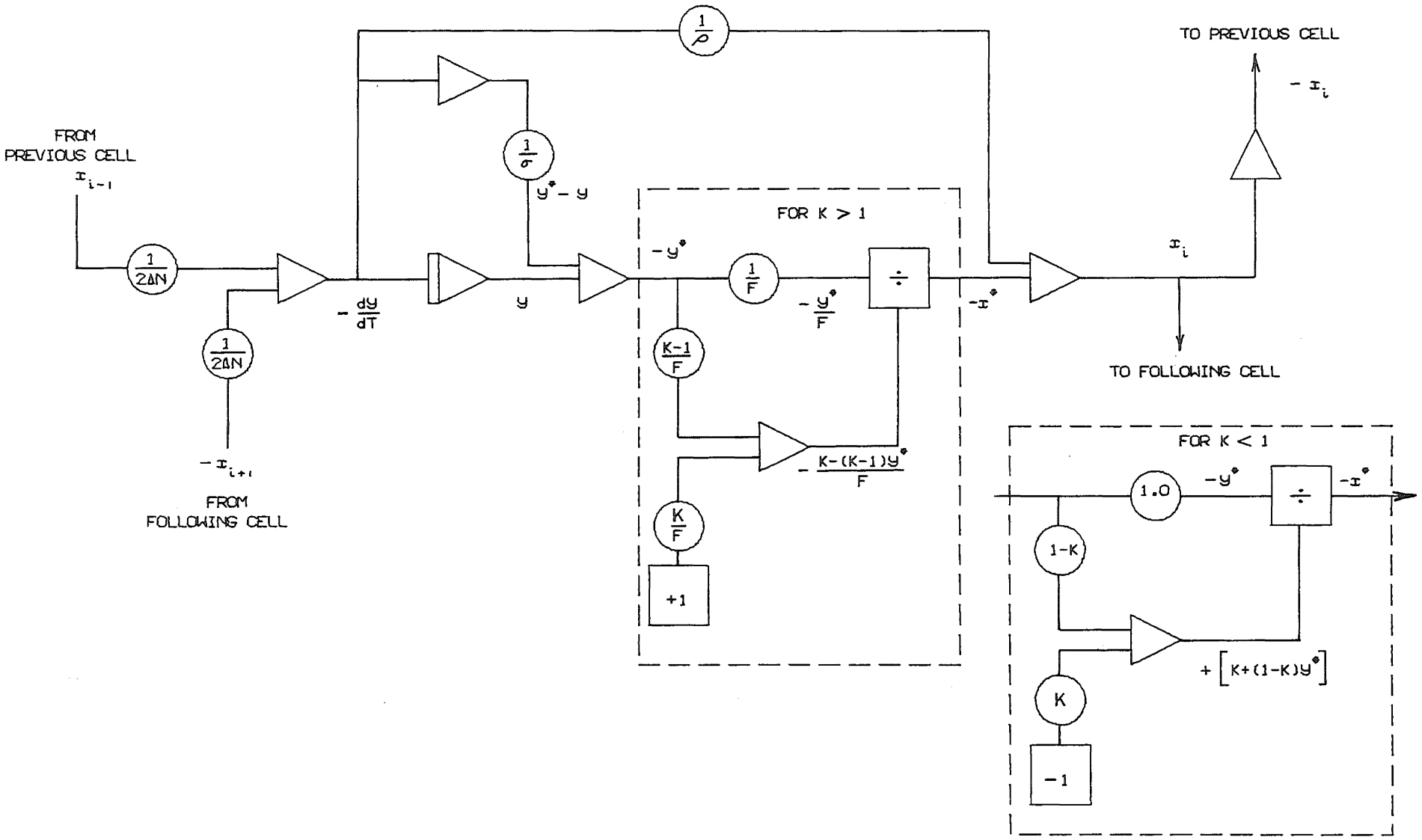


FIGURE 6-4. ANALOG COMPUTER SOLUTION FOR A SINGLE CELL.

$\Delta N = 2.0$, but smaller step-sizes were required for higher values of the mechanism parameter. Even with 10 cells, the number of transfer units in the simulation is quite restricted.

In addition to the accuracy constraints on the step-size, stability required that ΔN be greater than a half or one. The causes of this instability are the feedback loops that exist in the computer solution which contain no integrator. There are limiting gains for such loops (Wilkins, 1970) - the maximum gain for a loop containing n amplifiers is $\sec^n(\frac{\pi}{n})$. The gain in each cell, assuming K = 1, is $\frac{1}{2\Delta N} \cdot (\frac{1}{\rho} + \frac{1}{\sigma})$.

The largest loop in the system includes all the 10 cells, and the total loop gain is $(\frac{1}{2\Delta N})^{10} (\frac{1}{\rho} + \frac{1}{\sigma})^{10}$. The limiting gain for this system with so many amplifiers will be the asymptotic value of 1.0. Therefore

$$(\frac{1}{2\Delta N})(\frac{1}{\rho} + \frac{1}{\sigma}) < 1$$

$$\therefore \quad \Delta N > \frac{1}{2}(\frac{1}{\rho} + \frac{1}{\sigma})$$

The limiting values of the step-size depend on ρ, σ and hence on ξ as follows:-

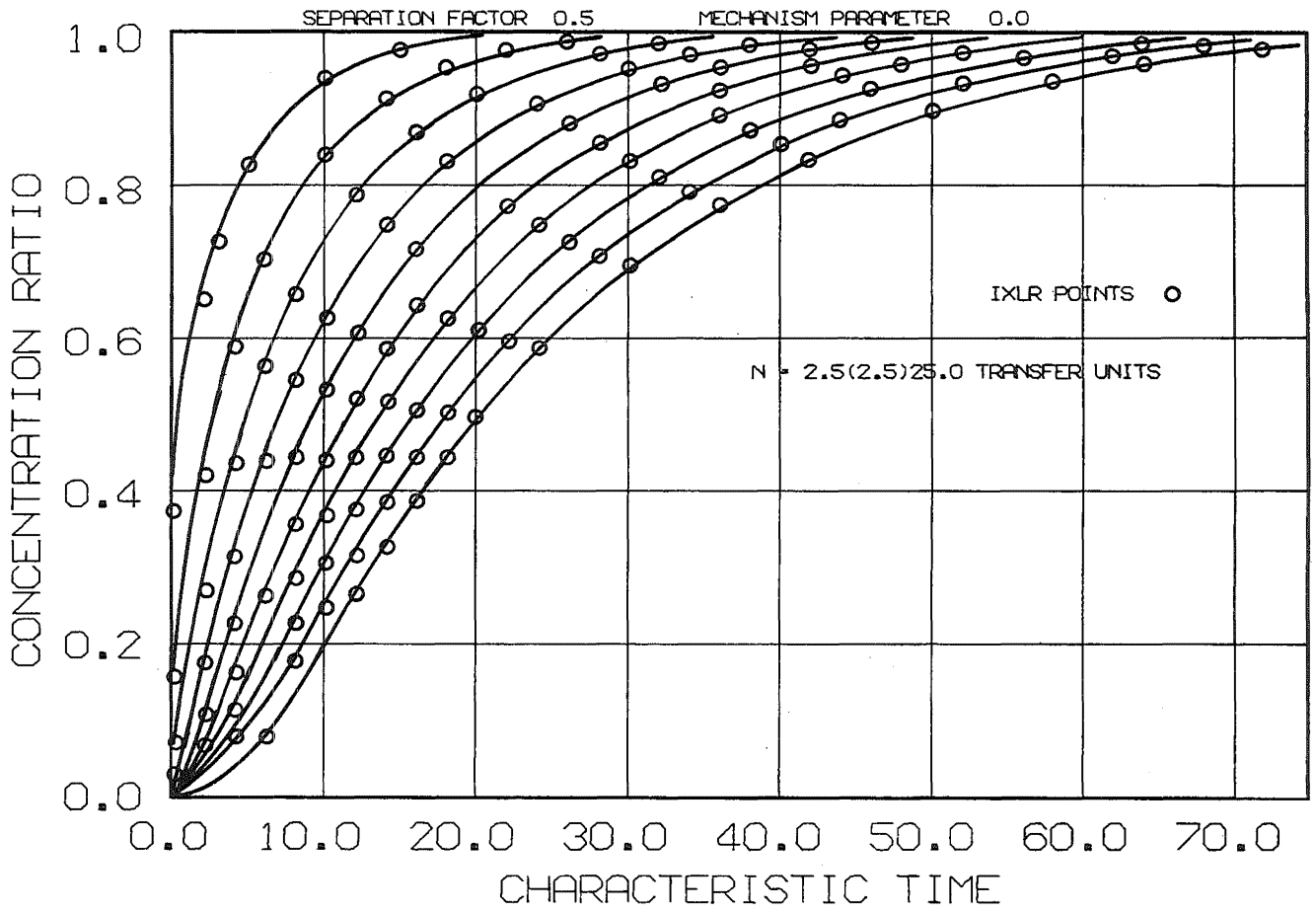
ξ	ΔN_{min}
0.0	½
1.0	1.0
∞	½

This is in good agreement with experience.

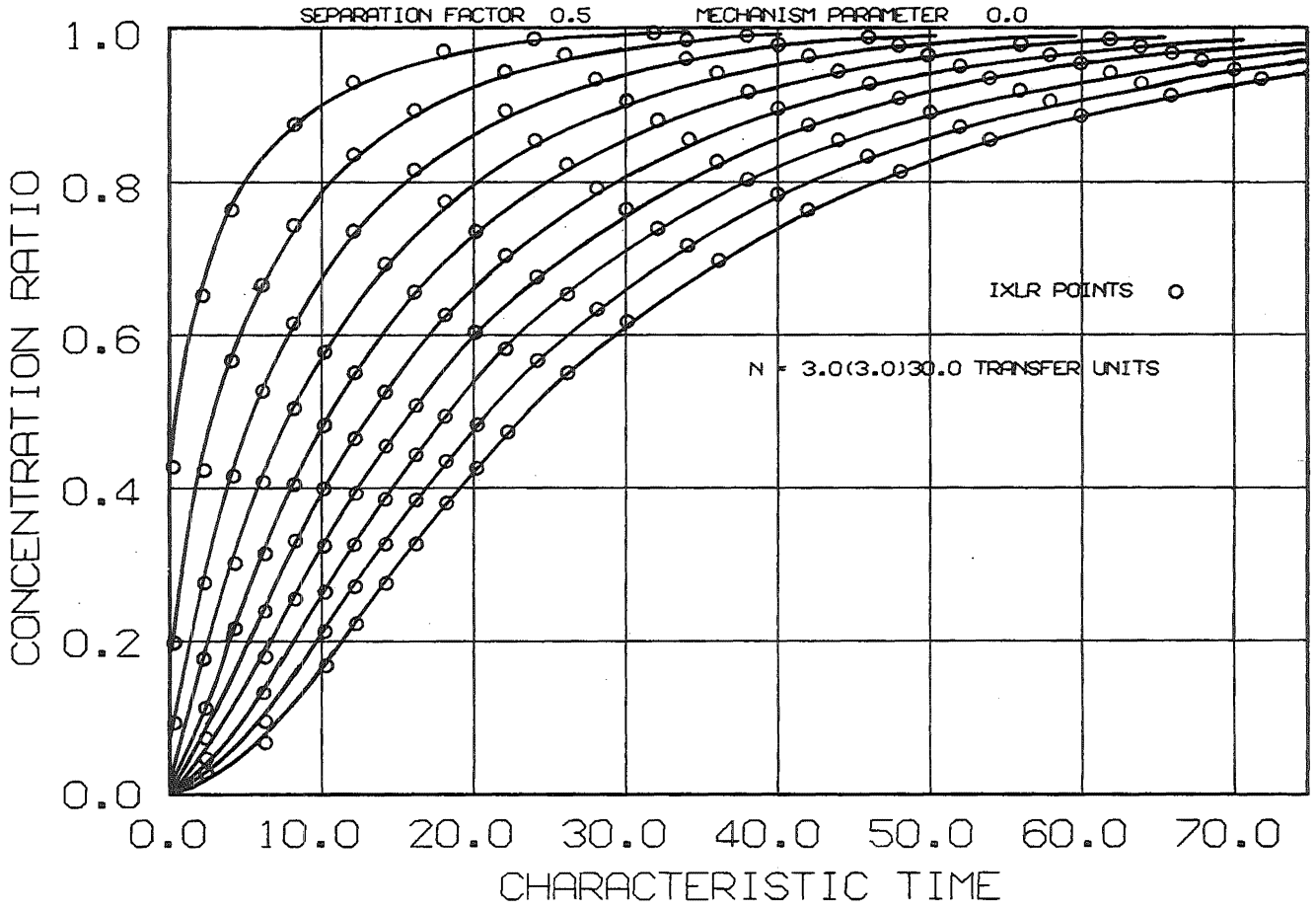
Graphs 6-2 to 6-7 are a selection of results for K = 0.5, 1.0, 1.2. These are direct copies of the analogue computer output to the XY-plotter.
Points from the digital computer program are superimposed. The agreement in almost all cases is within the ± 0.01 accuracy in the solution concentration ratio expected from the analogue computer solution.

6-4 A Comparison between the Digital and Analogue Computer Solutions for IXLR

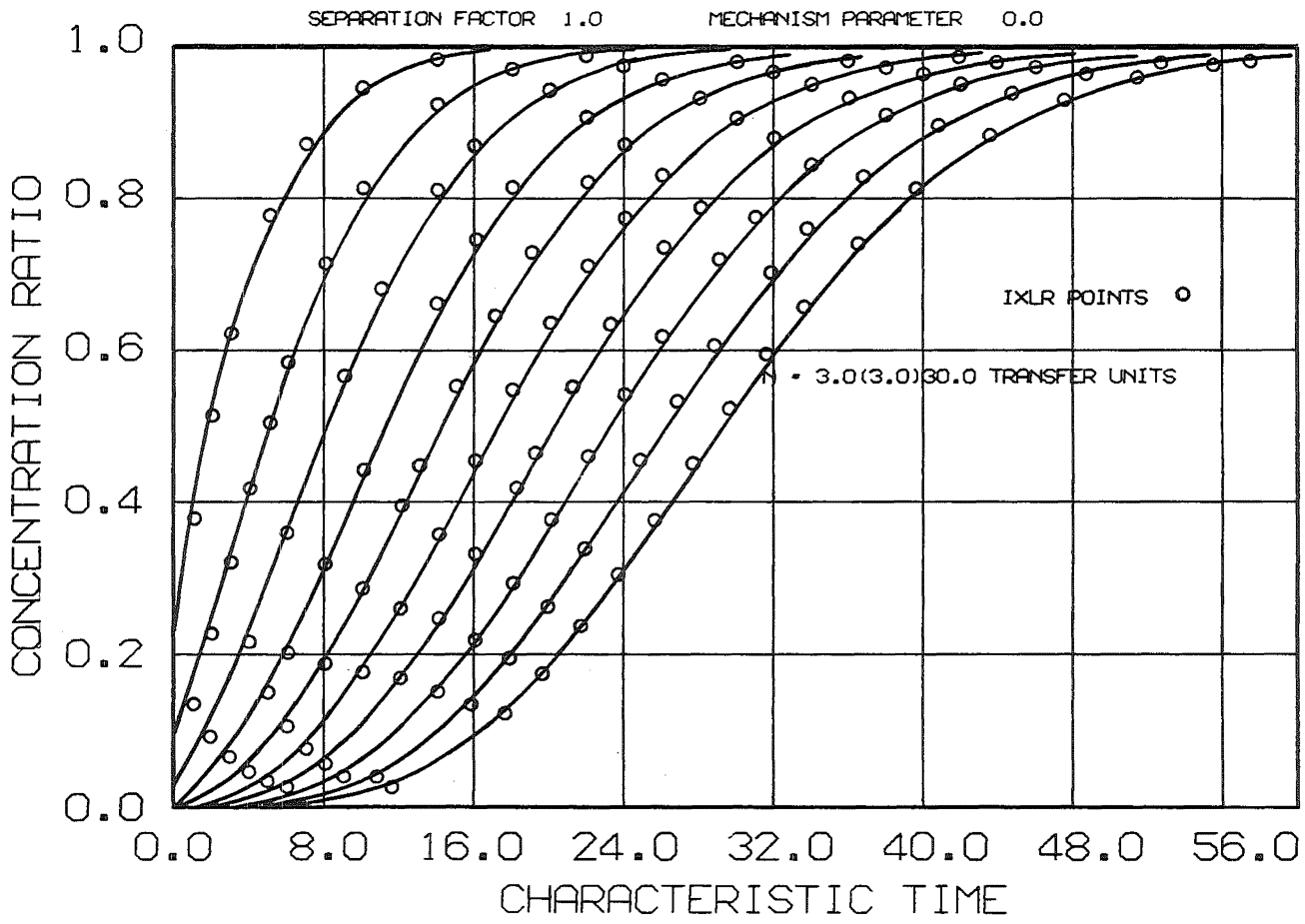
In most cases, there is no choice, and the ion exchange simulation must be performed on the computer available. The probability is that



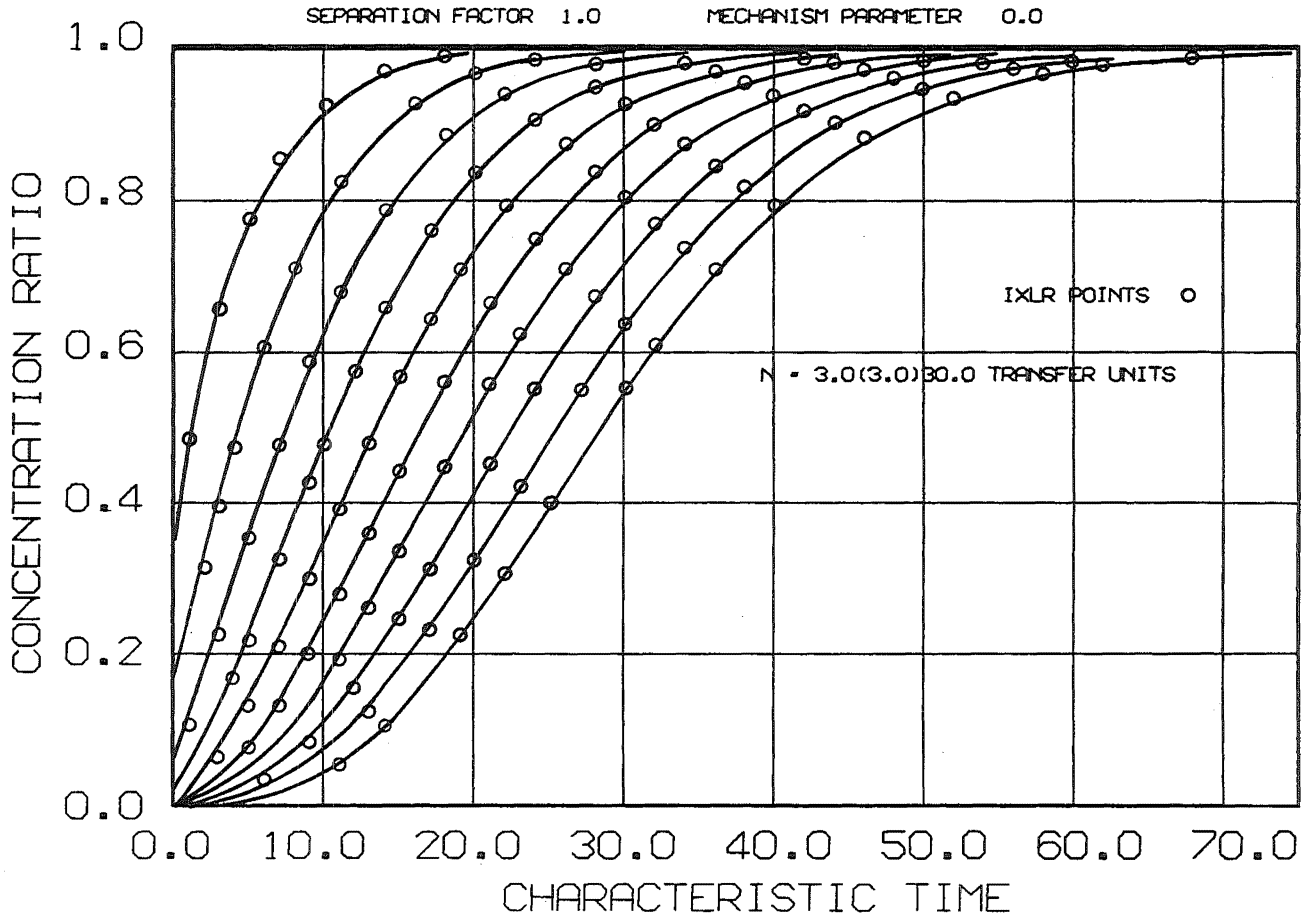
GRAPH 6-2. BREAKTHROUGH CURVES FROM THE ANALOG COMPUTER SOLUTION AIXLR COMPARED WITH DIGITAL COMPUTER RESULTS FROM IXLR



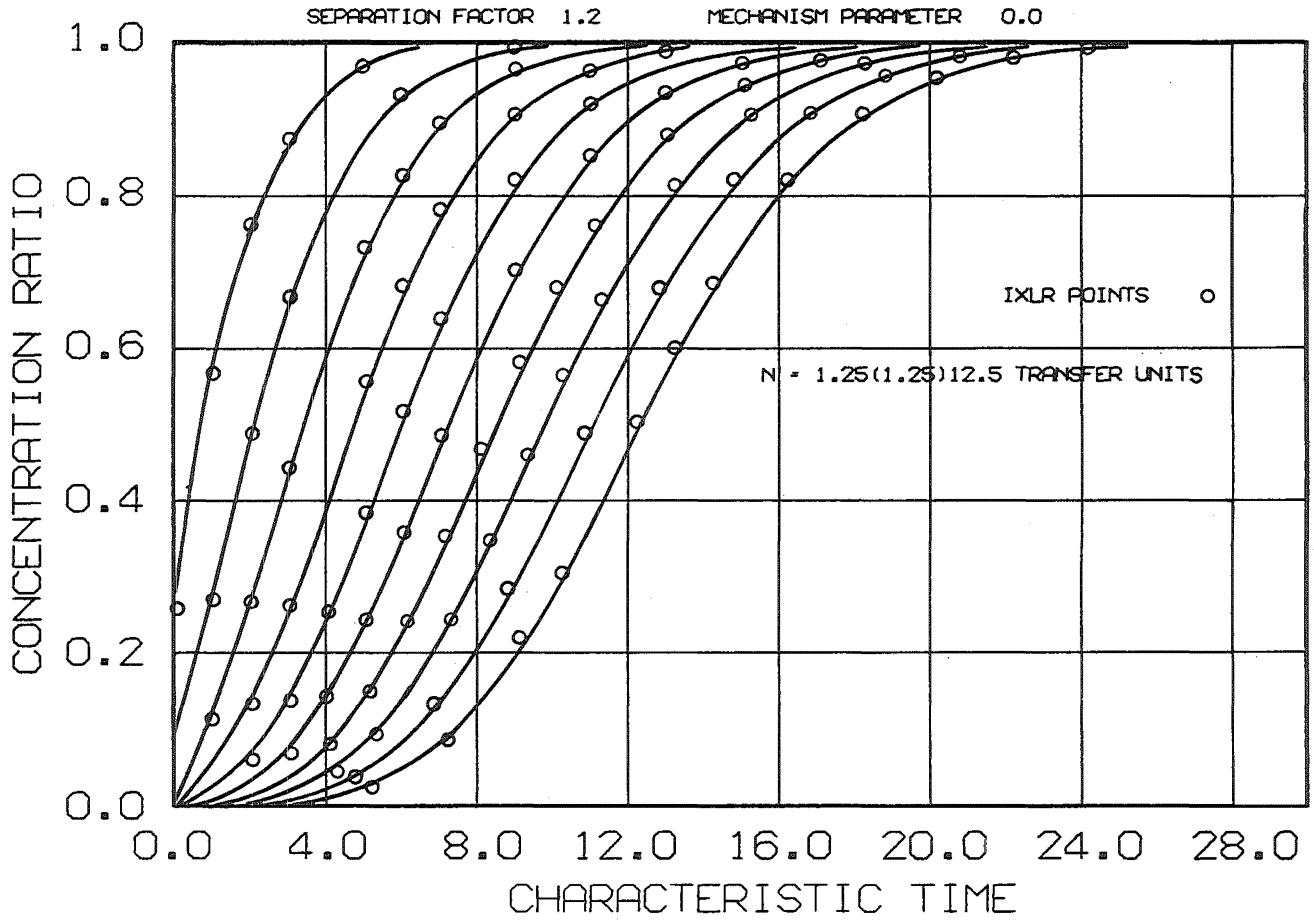
GRAPH 6-3. BREAKTHROUGH CURVES FROM THE ANALOG COMPUTER SOLUTION AIXLR COMPARED WITH DIGITAL COMPUTER RESULTS FROM IXLR



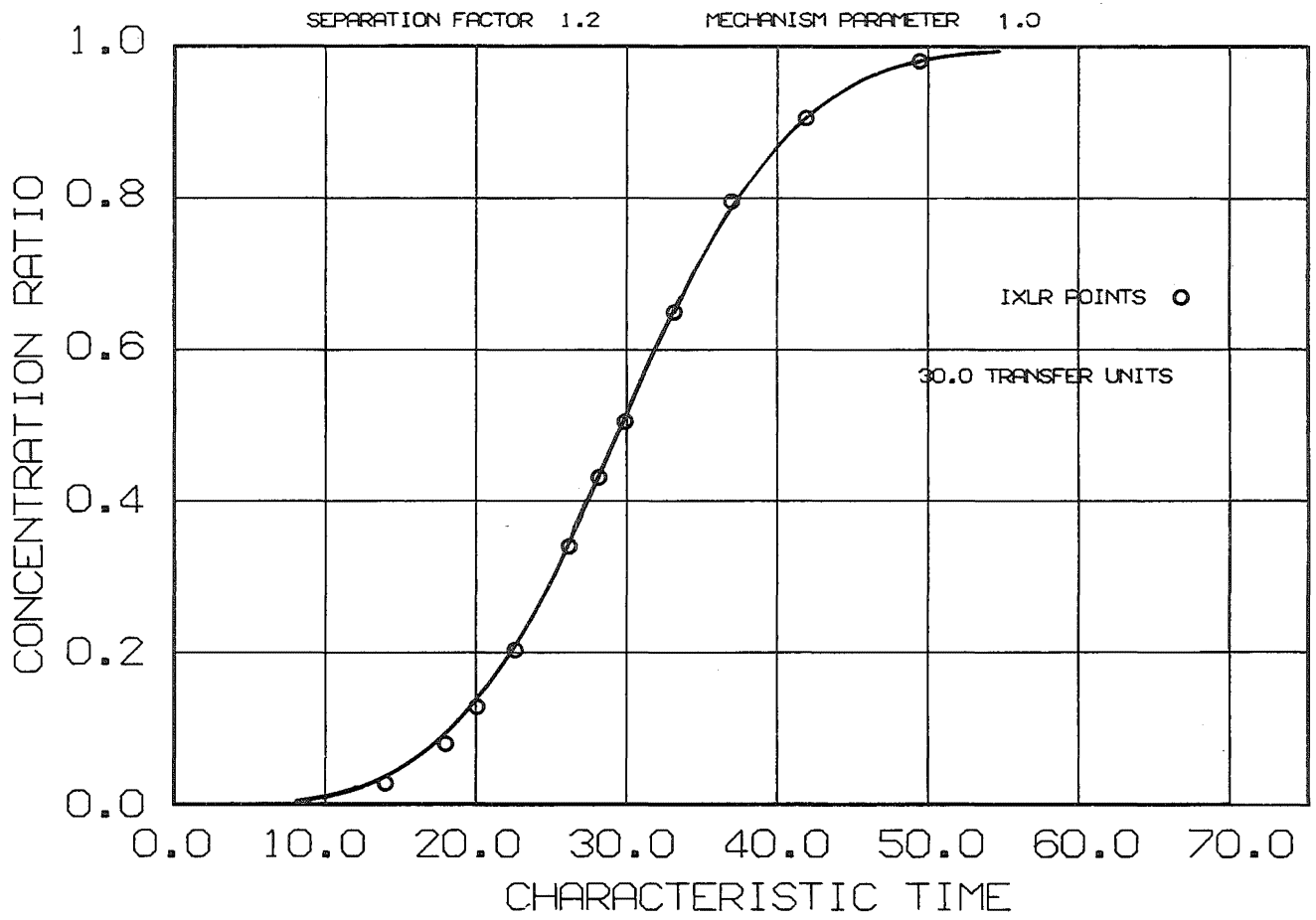
GRAPH 6-4. BREAKTHROUGH CURVES FROM THE ANALOG COMPUTER SOLUTION AIXLR COMPARED WITH DIGITAL COMPUTER RESULTS FROM IXLR



GRAPH 6-5. BREAKTHROUGH CURVES FROM THE ANALOG COMPUTER SOLUTION AIXLR COMPARED WITH DIGITAL COMPUTER RESULTS FROM IXLR



GRAPH 6-6. BREAKTHROUGH CURVES FROM THE ANALOG COMPUTER SOLUTION AIXLR COMPARED WITH DIGITAL COMPUTER RESULTS FROM IXLR



GRAPH 6-7. BREAKTHROUGH CURVES FROM THE ANALOG COMPUTER SOLUTION AIXLR COMPARED WITH DIGITAL COMPUTER RESULTS FROM IXLR

this will be a digital computer. The analogue computer solution, if performed in parallel, requires so much computing equipment even for a small column, that most analogue computers would be too small. Chapters 8 and 9 discuss a serial hybrid computer method for the more complex IXM model which obviates the need for an excessively large analogue computer.

The advantage of the analogue computer for this simulation was the ease with which a method of solution could be devised and correct results obtained.

The digital computer method had the advantage that once programmed it was easier to use. Data cards were added to a deck and the computing job handed to an operator. The analog computer was driven "hands-on", and required potentiometer setting and a sequence of checks before each run.

The computing speed of the analog computer was undoubtedly faster, but could not be utilised since to produce permanent output the speed of the XY-plotter was limiting.

Neither method had stability problems. The analog solution had difficulty in producing results for very favourable equilibrium. While the digital computer method was capable of greater precision, results from the analog were as accurate as experimental results.

Overall, with the program developed, the digital computer solution is preferable.

CHAPTER 7

THE FICKIAN PARTICLE DIFFUSION MODEL (IXM) - DIGITAL COMPUTER SOLUTION

Chapters 5 and 6 discussed the model IXLR which described fixed-bed ion exchange in terms of a linear particle-phase mass transfer rate expression. In this chapter, the model IXM is formed using the fickian diffusion equation. The computed values from IXM and IXLR are not significantly different.

7-1 The Equations of IXM

The equations of the model IXM are listed in Table 7-1. The concentration in the particle now becomes a function of the resin radius, $y(r)$, with an average value, $\bar{y}$.

The solution-side equations are as in IXLR - a hyperbolic partial differential equation in N and T with a linear rate equation. The particle-side equations are more complex - now a parabolic partial differential equation in R and T. These equations are related through the surface equilibrium.

However, the method of solution of IXM follows IXLR with the solution-side mass balance being solved by the method of characteristics and the rate, $d\bar{y}/dT$, being evaluated in a sub-program which solves the diffusion equation.

7-2 Initial and Boundary Conditions

The initial conditions for IXM are the same as those for IXLR in that the column is assumed initially free of solute ($y = 0$ for all N and all R at $T = 0$). The boundary conditions are those of constant feed composition ($x = 1.0$ at $N = 0$ for all $T > 0$). A new boundary condition is introduced to reflect the assumption of spherical symmetry in the resin particle ($\partial y/\partial R = 0$ at $R = 0$ for all N and T). This assumption requires that the particle diameter be small in comparison to the width of the reaction zone in the column so that the solution concentration can be taken as constant around the particle.

Source	Physical Form	General Form	
Solution mass balance, Eqn 2-11	$\frac{\partial x}{\partial t} + \frac{Q}{\varepsilon C_o}\frac{\partial \bar{y}}{\partial t} + \frac{v}{\varepsilon}\frac{\partial x}{\partial z} = 0$	$\frac{\partial x}{\partial N} + \frac{\partial \bar{y}}{\partial T} = 0$	(7-1)
Solution rate, Eqn 2-8.	$\frac{\partial y}{\partial t} = k_f(x - x^*)$	$\frac{\partial y}{\partial T} = \rho(x - x^*)$	(7-2)
Particle rate, Eqn 2-5.	$\frac{\partial y}{\partial t} = D_p(\frac{\partial^2 y}{\partial r^2} + \frac{2}{r}\frac{\partial y}{\partial r})$	$\frac{\partial y}{\partial T} = \sigma(\frac{\partial^2 y}{\partial R^2} + \frac{2}{R}\frac{\partial y}{\partial R})$	(7-3)
Particle mass balance, Eqn 2-12	$\bar{y} = \frac{24}{d_p{}^3}\int_o^{d_p/2} r^2 y dr$	$\bar{y} = 3\int_o^1 R^2\, y dR$	(7-4)
Equilibrium, Eqn 2-4.	$\frac{y^*}{1 - y^*} = K\frac{x^*}{1 - x^*}$	$\frac{y^*}{1 - y^*} = K\frac{x^*}{1 - x^*}$	(7-5)

Nomenclature (additional to Table 5-1)

d_p Particle diameter (L)

D_p Particle diffusivity ($L^2\ T^{-1}$)

k_p Equivalent particle mass transfer coefficient, $\frac{60D_p}{d_p{}^2}$

r Radial distance in particle (L)

R Fractional radial distance, $\frac{2r}{d_p}$

TABLE 7-1. Equations and nomenclature for the digital computer model, IXM.

7-3 Numerical Method of Solution

Equation 7-1 is solved by the method of characteristics, using Heun's method (Section 5-3) to provide values of x and $\bar{y}$ at mesh points in the N,T independent variable plane. The rate, $\partial\bar{y}/\partial T$, is calculated at each point using the RATE subprogram, Figure 7-1. The concentration profile y(R) is represented by the values,

$$y_i \quad i = 1,2,\cdots n_r+1$$

which are equally spaced over n_r radial elements, Figure 7-2.

The new concentration profile at $T + \Delta T$ is calculated from the profile at T, solving Eqn 7-3 using the Crank-Nicholson method (Lapidus, 1962, page 162). Appendix 7A shows that this reduces to solving the set of n_r linear algebraic equations:-

$$[-(6s+1)y_1 + 6sy_2]_{T+\Delta T} = -[-(6s-1)y_1 + 6sy_2]_T \tag{7-6}$$

$$[s\frac{(i-2)}{(i-1)}y_{i-1} - (2s+1)y_i + s\frac{i}{(i-1)}y_{i+1}]_{T+\Delta T}$$

$$= -[\frac{s}{i-1}(iy_{i+1} + (i-2)y_{i-1}) - (2s-1)y_i]_T \tag{7-7}$$

where $i = 2,3\cdots n_r$ and where $s = \frac{\sigma \cdot \Delta T}{30(\Delta R)^2}$.

The remaining equation required to solve for the n_{r+1} variables

$$y_i \quad i = 1,2,3\cdots n_r,\ n_r+1.$$

is the particle mass balance, Eqn 7-4, using Simpson's rule (Lapidus, 1962, page 49) to express the integral as a summation

$$[4(y_2 + 3^2y_4 + 5^2y_6 \cdots) + 2(2^2y_3 + 4^2y_5 \cdots)$$

$$+ n_r{}^2y_{n_r+1}]_{T+\Delta T} = n_r{}^3\bar{y} \tag{7-8}$$

Minor modification of this set of equations allows them to be expressed in tri-diagonal form which can be efficiently solved using

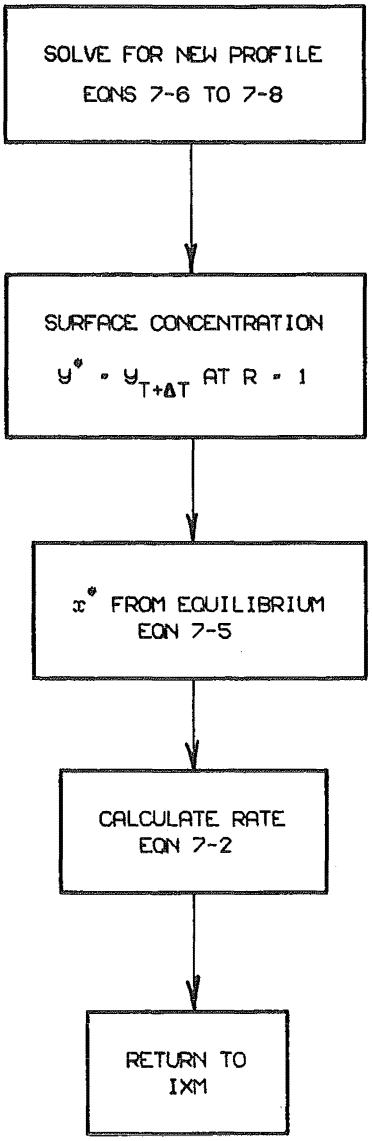


FIGURE 7-1. GENERAL FLOW SHEET FOR RATE

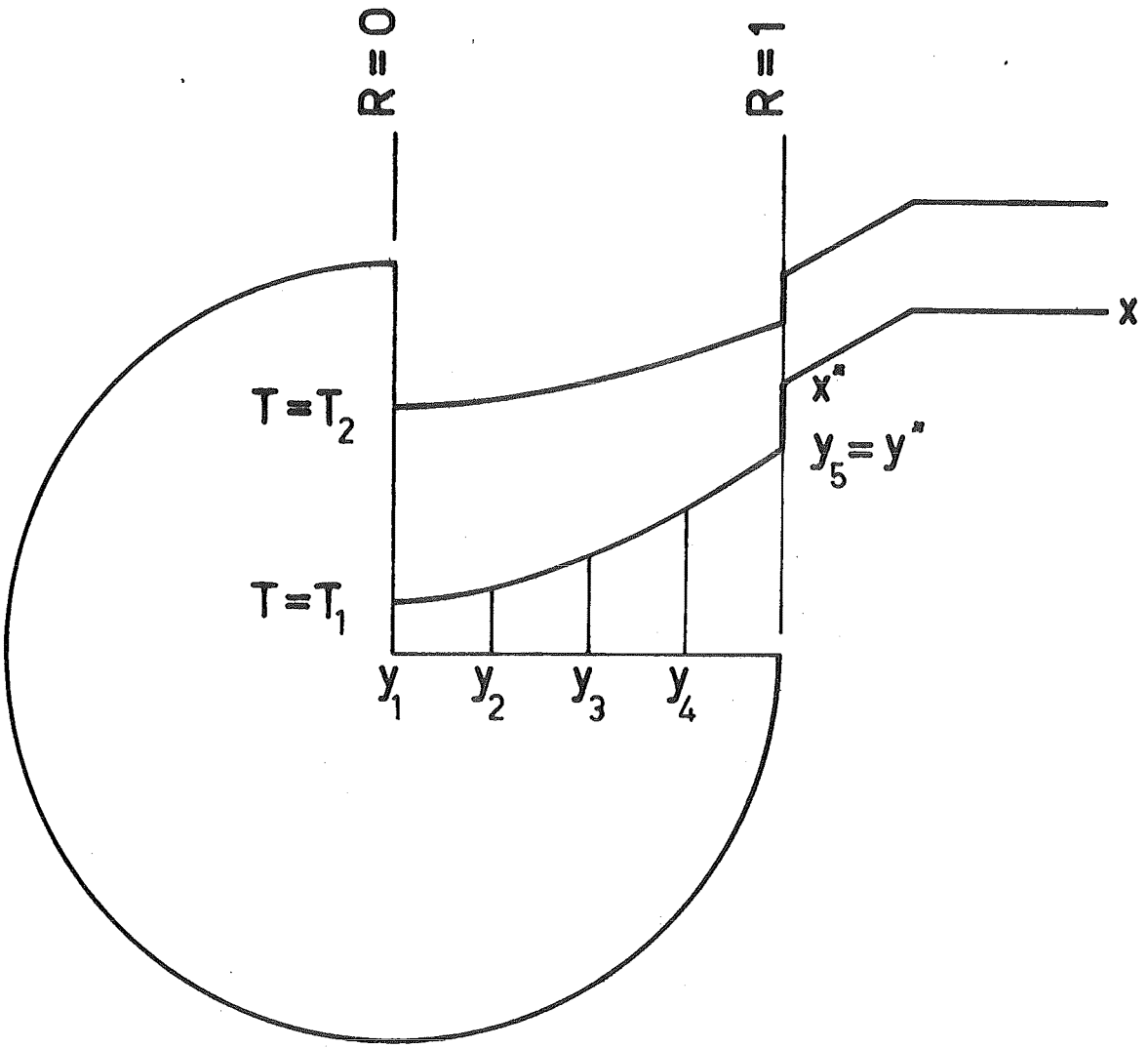


FIGURE 7-2. PARTICLE CONCENTRATION PROFILES AT TWO VALUES OF THE CHARACTERISTIC TIME.

the Thomas method (Lapidus, 1962, page 254).

With particle concentration profile established, the surface concentration is available:-

$$y^*_{T+\Delta T} = y_{n_r+1,T+\Delta T}$$

The solution concentration ratio at the interface is in equilibrium

$$x^*_{T+\Delta T} = \frac{y^*}{y^* + K(1 - y^*)} \qquad (7\text{-}9)$$

and the rate can be calculated:-

$$\left(\frac{d\bar{y}}{dT}\right)_{T+\Delta T} = \rho\,(x_{T+\Delta T} - x^*_{T+\Delta T}) \qquad (7\text{-}10)$$

The computer program IXM is listed in Appendix 7B with some sample results. The method of solution does not require iteration nor numerical differentiation.

7-4 Program Verification

The results of the program IXM can be compared with those of Rosen (1954) for linear equilibrium. Exactly the same equations are solved. However, Rosen's results are sparse, and Appendix 9B presents a program, BGP, which has been used to produce the values for comparison in Tables 7-2, 7-3 and 7-4. The program is based on an extension of Rosen's work (Babcock, Green and Perry, 1966) to include axial dispersion if required.

As the step-size is reduced, the results of IXM tend to Rosen's results within 0.002, the accuracy of the BGP program, and indicate its correctness, at least for linear equilibrium.

Verification for non-linear equilibrium is more difficult. However, the calculation of RATE for IXM does not use any special relation for K = 1, and consequently the program is generally proven provided the equilibrium calculation is correct for all values of the separation factor. Values of x* and y* are listed in Table 7-5 and the separation factors calculated from them are the specified value to the five decimal places printed. The values shown in Appendix 7B are correctly calculated for K = 1.0.

x values at T = 2,6,10,14,20

N = 10	NR	IXM 4	IXM 6	IXM 10	BGP
		.043	.043	.041	.055
		.308	.309	.309	.302
ΔN = 0.25		.580	.582	.584	.571
		.774	.775	.776	.770
		.924	.923	.923	.925
		.051	.053	-	.055
		.303	.304	-	.302
ΔN = 0.125		.574	.574	-	.571
		.772	.771	-	.770
		.925	.925	-	.925
		.052	-	-	.055
		.302	-	-	.302
ΔN = 0.0625		.573	-	-	.571
		.771	-	-	.770
		.925	-	-	.925

x values at T = 30,40,50,60,70

N = 50	NR	IXM 4	IXM 6	IXM 10	BGP
		.061	.061	.060	.060
		.254	.254	.255	.251
ΔN = 0.25		.535	.536	.537	.531
		.774	.774	.775	.772
		.912	.912	.912	.913
		(203 sec)	(269 sec)	(395 sec)	
		.062	.063	-	.060
		.252	.253	-	.251
ΔN = 0.125		.533	.532	-	.531
		.773	.773	-	.772
		.913	.912	-	.913
		(619 sec)	(859 sec)		
		.062	-	-	.060
		.252	-	-	.251
ΔN = 0.0625		.532	-	-	.531
		.773	-	-	.772
		.912	-	-	.913
		(2250 sec)			

The bracketed quantities are computation times to 50 transfer units.

TABLE 7-2 Comparison of IXM and BGP results

K = 1.0 ξ = 1.0 N = 10.0,50.0

x values at T = 2,6,10,14,20				
	IXM			BGP
NR	4	6	10	
	.014	.014	-	.014
	.205	.205	-	.204
ΔN = 0.125	.548	.548	-	.547
	.814	.814	-	.813
	.969	.969	-	.969
	(37 sec)	(50 sec)		
	.014	.014	.014	.014
	.204	.204	.204	.204
ΔN = 0.0625	.548	.548	.548	.547
	.813	.813	.813	.813
	.969	.969	.969	.969
	(128 sec)	(177 sec)	(287 sec)	

The bracketed quantities are computation times to 10 transfer units

TABLE 7-3 Comparison of IXM and BGP results.

K = 1.0 ξ = 10.0 N = 10.0

x values at T = 2,6,10,14,20				
	IXM			BGP
NR	4	6	10	
	.015	-	-	.022
	.258	-	-	.255
ΔN = 0.1	.571	-	-	.566
	.794	-	-	.791
	.946	-	-	.946
	(57 sec)			
	.018	.018	.018	.022
	.256	.256	.257	.255
ΔN = 0.05	.568	.568	.568	.566
	.792	.792	.792	.791
	.946	.946	.947	.946
	(204 sec)	(244 sec)	(370 sec)	
	.020	.020	-	.022
	.256	.256	-	.255
ΔN = 0.025	.567	.567	-	.566
	.792	.792	-	.791
	.946	.946	-	.946
	(727 sec)			

The bracketed quantities are computation times to 10 transfer units.

TABLE 7-4. Comparison of IXM and BGP results.

K = 1.0 ξ = 0.5 N = 10.0

Other methods used to check IXLR (Section 5-4) have been applied to IXM, and have shown no inconsistency. A general test for the accuracy of the matrix inversion procedure is given by Eqn 7-8 which can be written for four radial elements

$$4y_2 + 8y_3 + 36y_4 + 16y^* = 64\bar{y} \qquad (7\text{-}11)$$

and values of $\bar{y}$ calculated from this equation are included in Table 7-5.

7-5 Step-size and Stability

Tables 7-2 to 7-7 show the effect of the step-size, ΔN, and the number of radial elements, n_r, on the results of the program IXM. The fixed relation

$$\Delta T = 2 \cdot \Delta N$$

was still used.

In all cases, four radial elements were adequate, and this is the minimum to use Simpson's rule for the quadrature (Eqn 7-4).

In comparison with IXLR, IXM is almost an order of magnitude slower. Tables 7-2 and 7-3 for linear equilibrium and the mechanism parameter 1.0 and 10.0 show that a step-size ΔN of 0.125 will give results generally within 0.002. However, when the particle phase resistance becomes controlling ($\xi < 0.3$) stability problems force the use of smaller step-sizes, down to $\Delta N = 0.01$ for $\xi = 0.1$.

Table 7-6 and 7-7 show similar results for non-linear equilibrium, and indicate that a step-size of $\Delta N = 0.125$ is still adequate, but perhaps with a slightly larger convergence error than for linear equilibrium.

In general, the step-size used to produce results from IXM was

$$\Delta N = \frac{0.125}{\rho}$$

to account for the smaller step-size required for values of the mechanism parameter less than one. Four radial elements have been used.

The stability problem arises from the calculation of y* from an equation such as Eqn 7-11

Equilibrium

Listed values (for K = 0.2)

x*	y*	Calculated values of K
.21038	.05059	.200015
.41648	.12491	.199989
.53302	.18586	.200004
.61262	.24029	.200001
.75133	.37666	.199994
.83387	.50097	.200002

Matrix Inversion

	Listed values				Calculated value of $\bar{y}$ (Eqn 7-11)	
T	y_2	y_3	y_4	y_5	$\bar{y}$	
30	.0342	.0377	.0439	.0533	.0449	.04487
40	.1775	.1875	.2046	.2294	.2070	.20697
50	.4378	.4511	.4732	.5042	.4760	.47598
60	.7004	.7109	.7282	.7518	.7302	.73020
70	.8857	.8910	.8996	.9112	.9006	.90056

These values are taken from Appendix 7B

TABLE 7-5. Verification of the equilibrium and matrix inversion calculations in IXM.

x values at T = 2,6,10,14,20		
N_R	4	6
$\Delta N = 0.125$	.012	.012
	.157	.158
	.540	.541
	.849	.850
	.979	.979
	(41 sec)	(57 sec)
$\Delta N = 0.0625$	.012	-
	.156	-
	.537	-
	.848	-
	.980	-
	(138 sec)	

The bracketed quantities are computation times to 10 transfer units

TABLE 7-6. Effect of step-size on IXM results with favourable equilibrium.

$K = 2.0$ $\xi = 1.0$ $N = 10.0$

x values at T = 1,2,5,10,20

NR	4	6	10
	.056	.055	.049
	.159	.157	.149
ΔN = 0.125	.389	.390	.391
	.632	.632	.633
	.864	.864	.864
	(37 sec)	(51 sec)	(82 sec)
	.066	.070	-
	.160	.162	-
ΔN = 0.0625	.387	.387	-
	.632	.631	-
	.863	.863	-
	(135 sec)	(191 sec)	

The bracketed quantities are computation times to 10 transfer units.

TABLE 7-7. Effect of step-size on IXM results with unfavourable equilibrium.

K = 0.5 ξ = 1.0 N = 10.0

$$y^* = 4\bar{y} - \tfrac{1}{4}y_2 - \tfrac{1}{2}y_3 - \frac{9}{4}y_4$$

For a large ΔT, the mass transferred can be large, corresponding to a large change in $\bar{y}$. The finite difference equations (Eqns 7-6, 7-7) depend more strongly on the previous profile than $\bar{y}$ and underestimate the y_i values. The resultant y* can become greater than 1.0, particularly with the subtraction involved. The error is reflected in the value of x* and magnified in the calculation of RATE by Eqn 7-2, where the subtraction will be of nearly equal quantities for small values of the mechanism parameter and large ρ.

Results are easily obtained for values of the mechanism parameter greater than 0.3.

Numerical solutions of parabolic partial differential equations characteristically provide stability problems of the type encountered here. Several other numerical methods claimed to be more stable have been used in place of the Crank-Nicholson method; the implicit method (Lapidus, 1962, page 161) and an alternating direction method (Liu, 1969). There was no improvement, supporting the argument that the problem does not lie with the parabolic equation, but rather between it and the hyperbolic partial differential equation.

This stability problem is analogous to that reported by McGreavy (1967) who used the differential form of the particle mass balance (Eqn 2-15). The advantages of the integrated form in computing time and therefore stability can be seen by a comparison with a result reported by McGreavy ($K = 1$, $\xi = 0.05$) requires 11 minutes on a KDF-9 computer. The IXM program on the IBM 360/44 used here required 82 seconds.

A comparison of the two computers:-

	KDF9	IBM 360/44
Add time	1 μsec	5.31 μsec
Multiply time	15-30 μsec	15.56 μsec
Access time	1.2 - 6.0 μsec	1.2 μsec

suggests a small inherent advantage to the IBM computer, but not enough to affect the conclusion that the integrated form of the particle mass balance is preferable.

7-6 The Comparison of IXM with IXLR

The comparison of the results of IXM with those of IXLR is the extension of a comparison between the J function and Rosen's integral to non-linear equilibrium. The difference is in the particle rate expression:-

J Function Linear rate expression Eqn 2-7 $\frac{\partial y}{\partial T} = k_p(y^*-y)$

Rosen Fickian rate expression Eqn 2-5 $\frac{\partial y}{\partial T} = D_p(\frac{\partial^2 y}{\partial R^2} + \frac{2}{R}\frac{\partial y}{\partial R})$

This comparison is shown in Graph 7-1 for a range of ξ and N values.

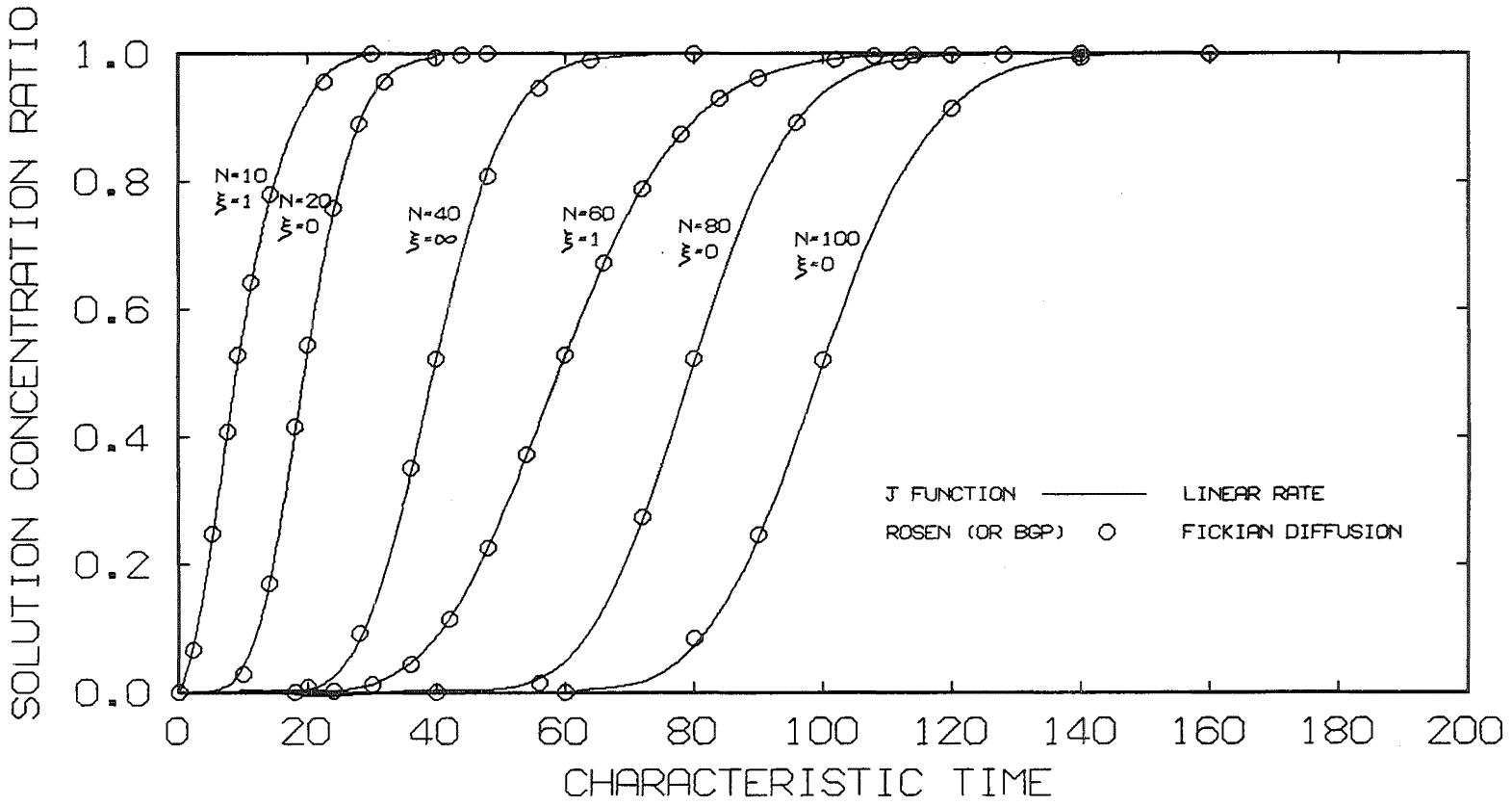
Graphs 7-2 to 7-10 compare the results of IXM and IXLR, for a range of ξ and K values. The difference is remarkably small.

The divergence between the two models will be greatest when rate is more significant than equilibrium (i.e. favourable equilibrium) and where the particle mass transfer effects are greatest (i.e. small ξ). Graph 7-2 for K = 2.0 and ξ = 0.3 shows a maximum difference of 0.01 in x occurring in both corners of the breakthrough curve, where the curvature is greatest and not dependent on the number of transfer units in the column.

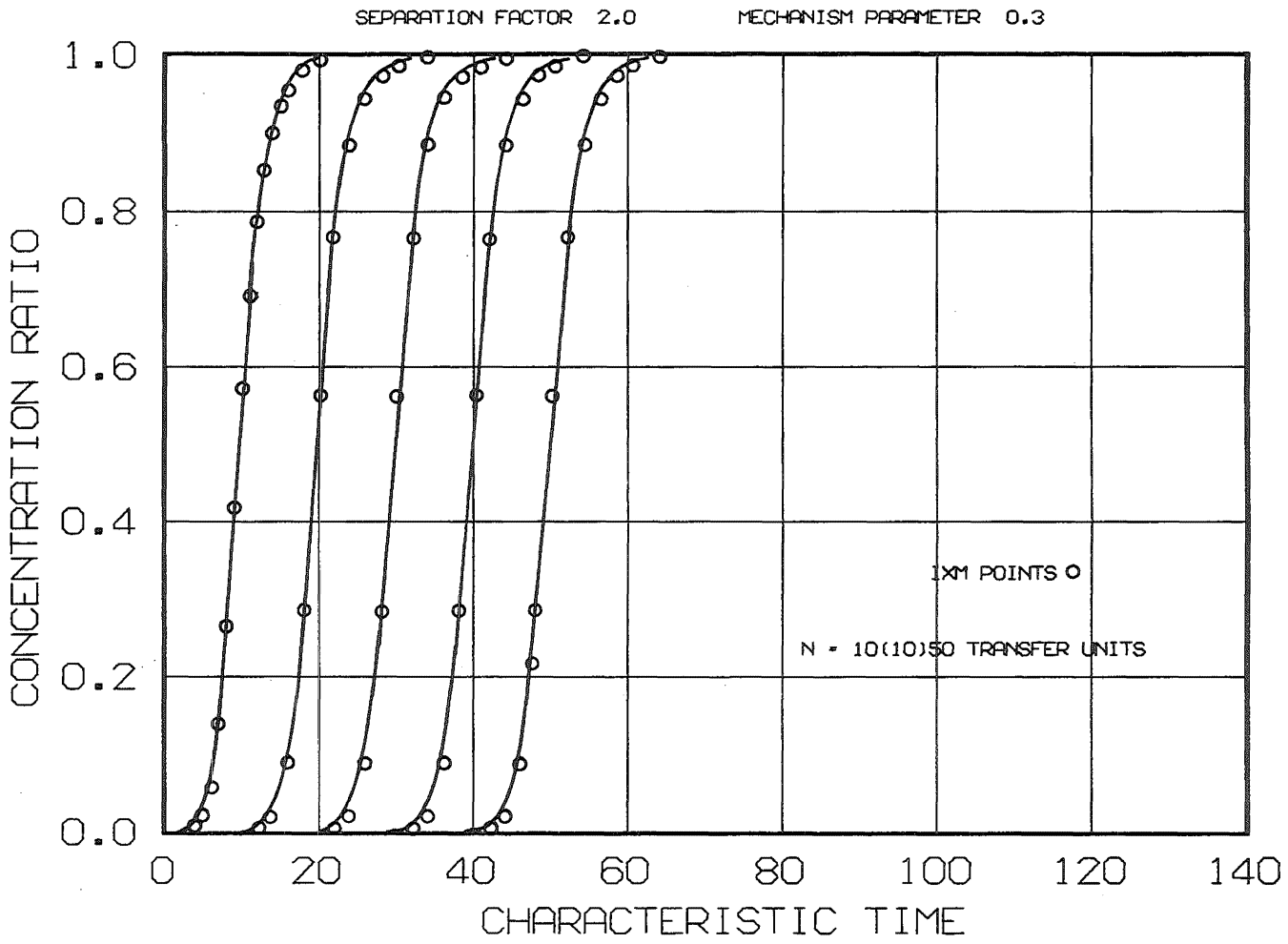
For most other cases, the divergence between IXM and IXLR is less than the resolution of the graphs and would not be significant for any practical purposes of fixed-bed, ion exchange column design or analysis. However, for batch operation, the particle rate expression may be more significant.

By the nature of numerical solution to the IXM equations, total film or particle mass transfer control (ξ = 0 or ∞) is not admissible, but this limiting behaviour will be approximated for sufficiently small (ξ < 0.3) or large (ξ > 3) values of the mechanism parameter. The numerical solution must proceed timewise at constant N, without the choice available in IXLR.

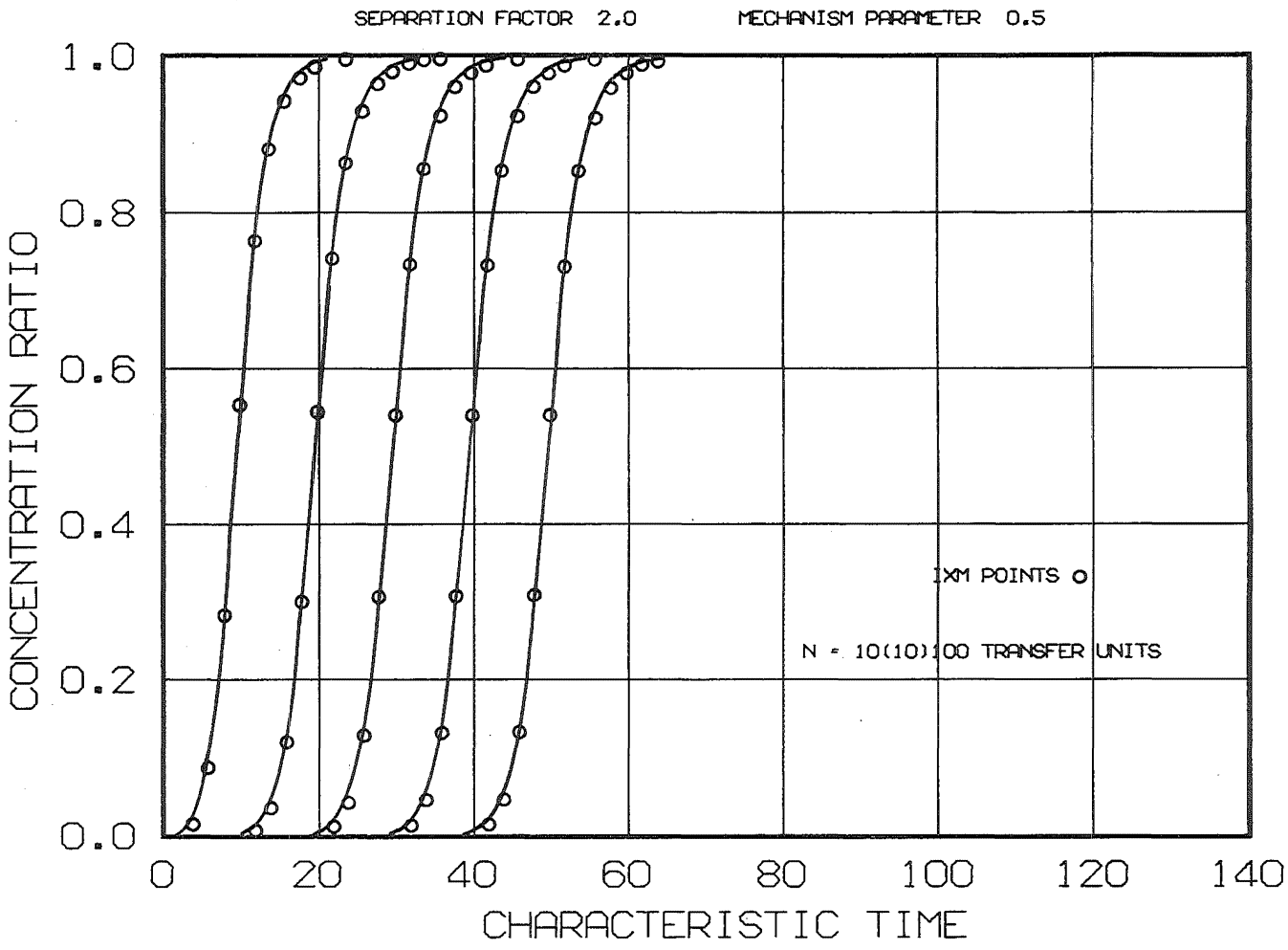
The results of IXM have not been compared with experimental data (for the RATE function modified to a concentration dependent separation factor) because the conclusions would echo those of IXLR.



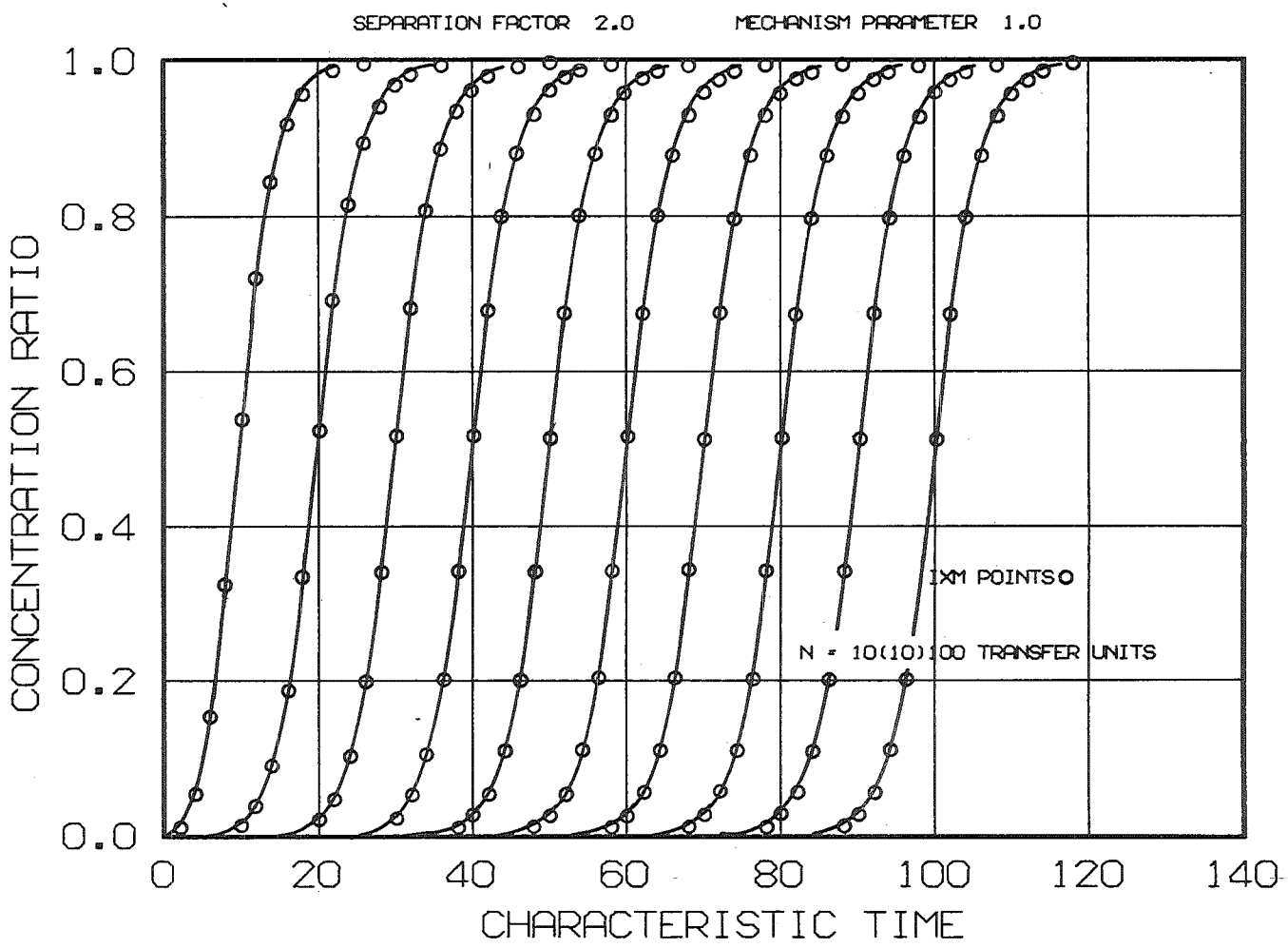
GRAPH 7-1. A COMPARISON BETWEEN THE J FUNCTION AND ROSEN'S (OR BGP) INTEGRATION, DIFFERING IN THE PARTICLE RATE EQUATION.



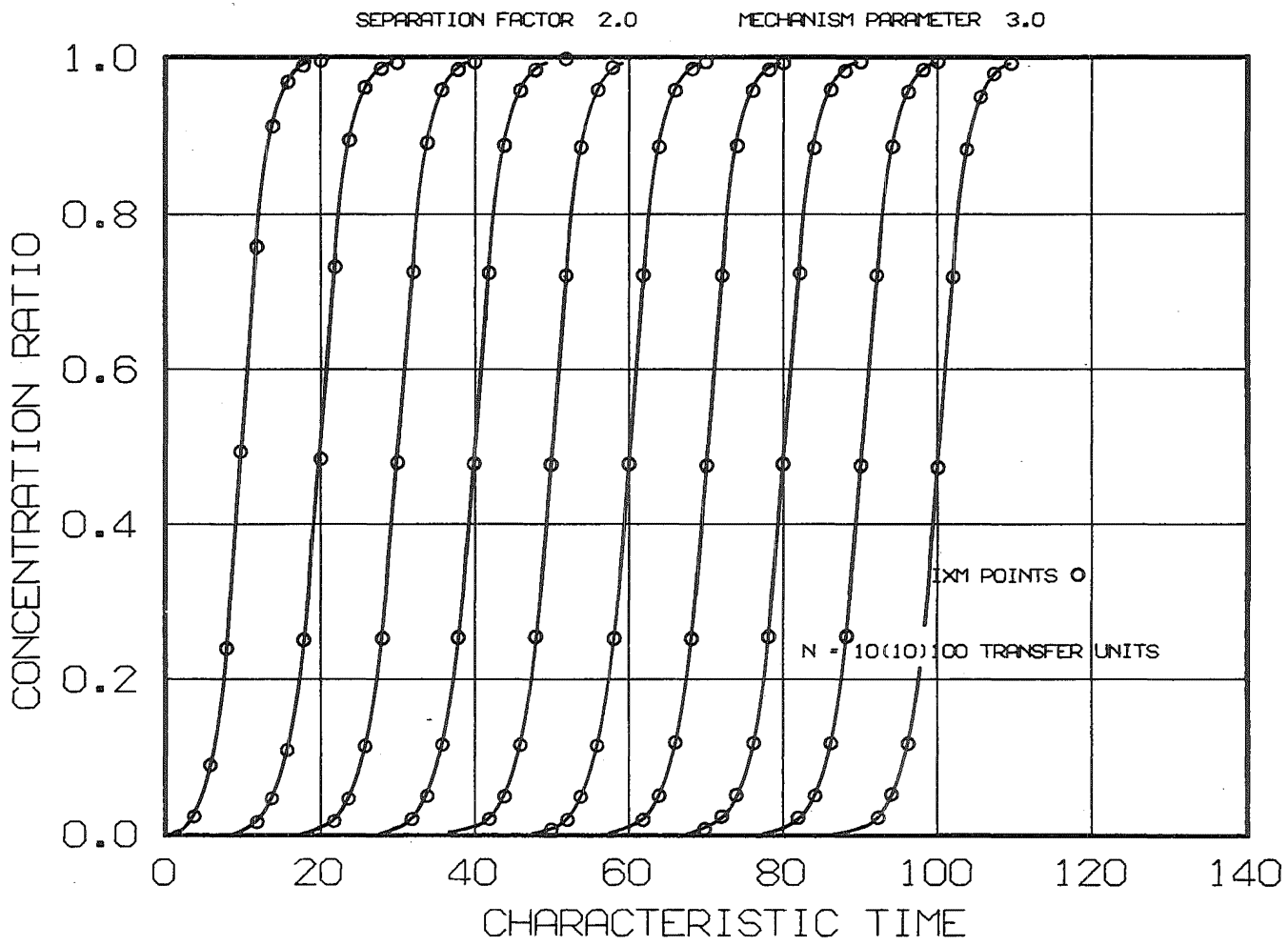
GRAPH 7-2. COMPUTED BREAKTHROUGH CURVES - IXM RESULTS COMPARED WITH IXLR CURVES.



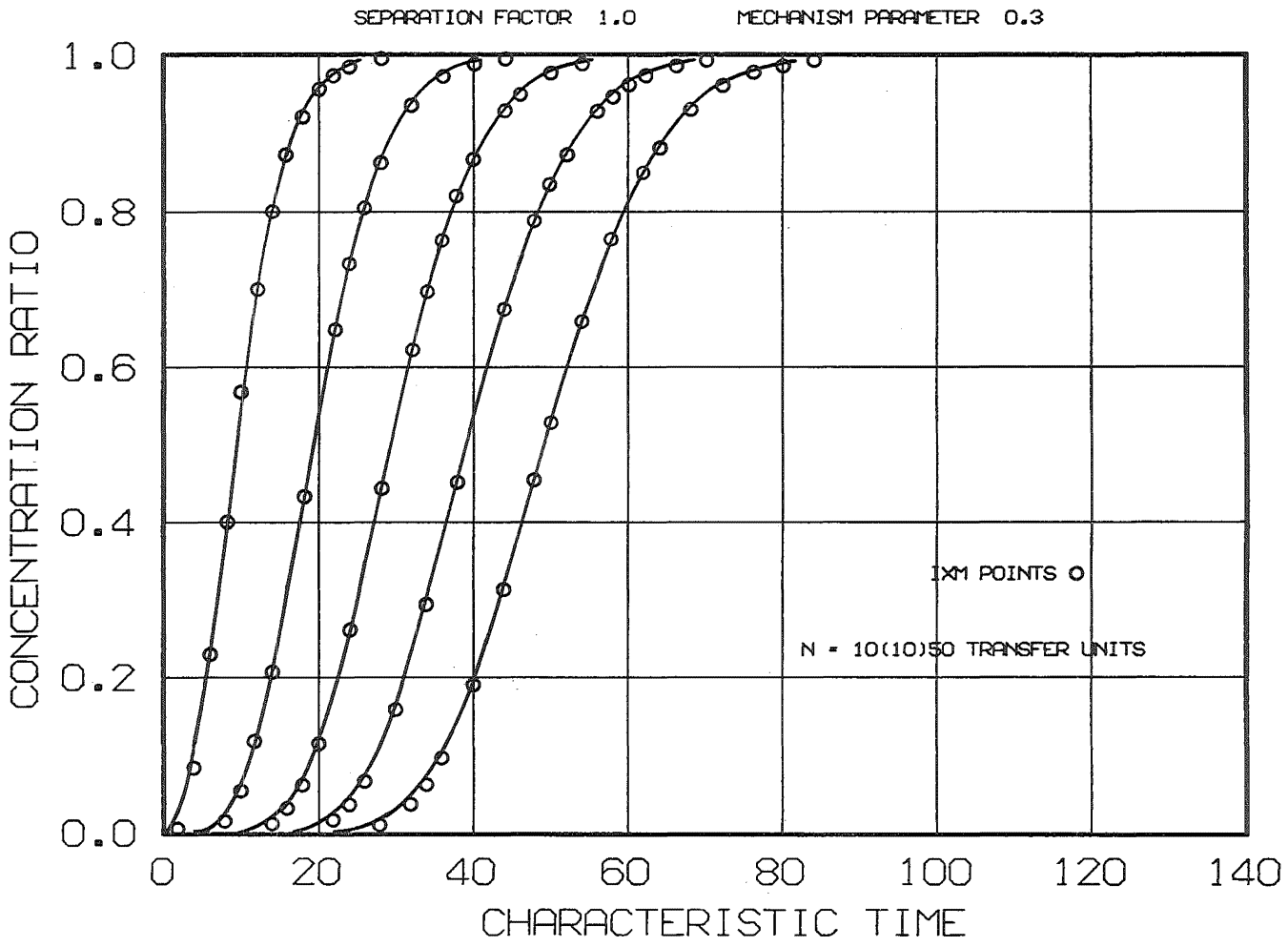
GRAPH 7-3. COMPUTED BREAKTHROUGH CURVES - IXM RESULTS COMPARED WITH IXLR CURVES.



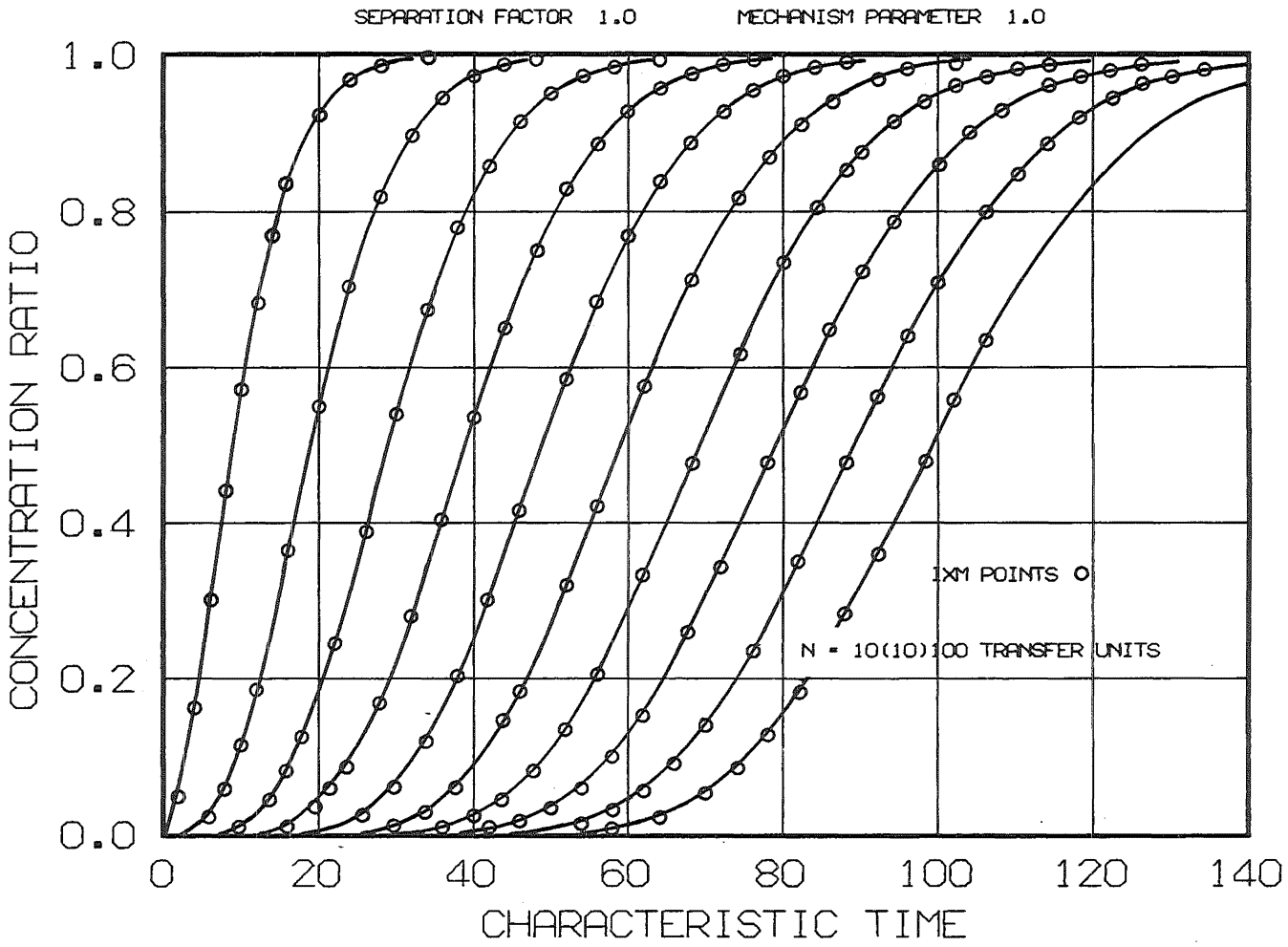
GRAPH 7-4. COMPUTED BREAKTHROUGH CURVES - IXM RESULTS COMPARED WITH IXLR CURVES.



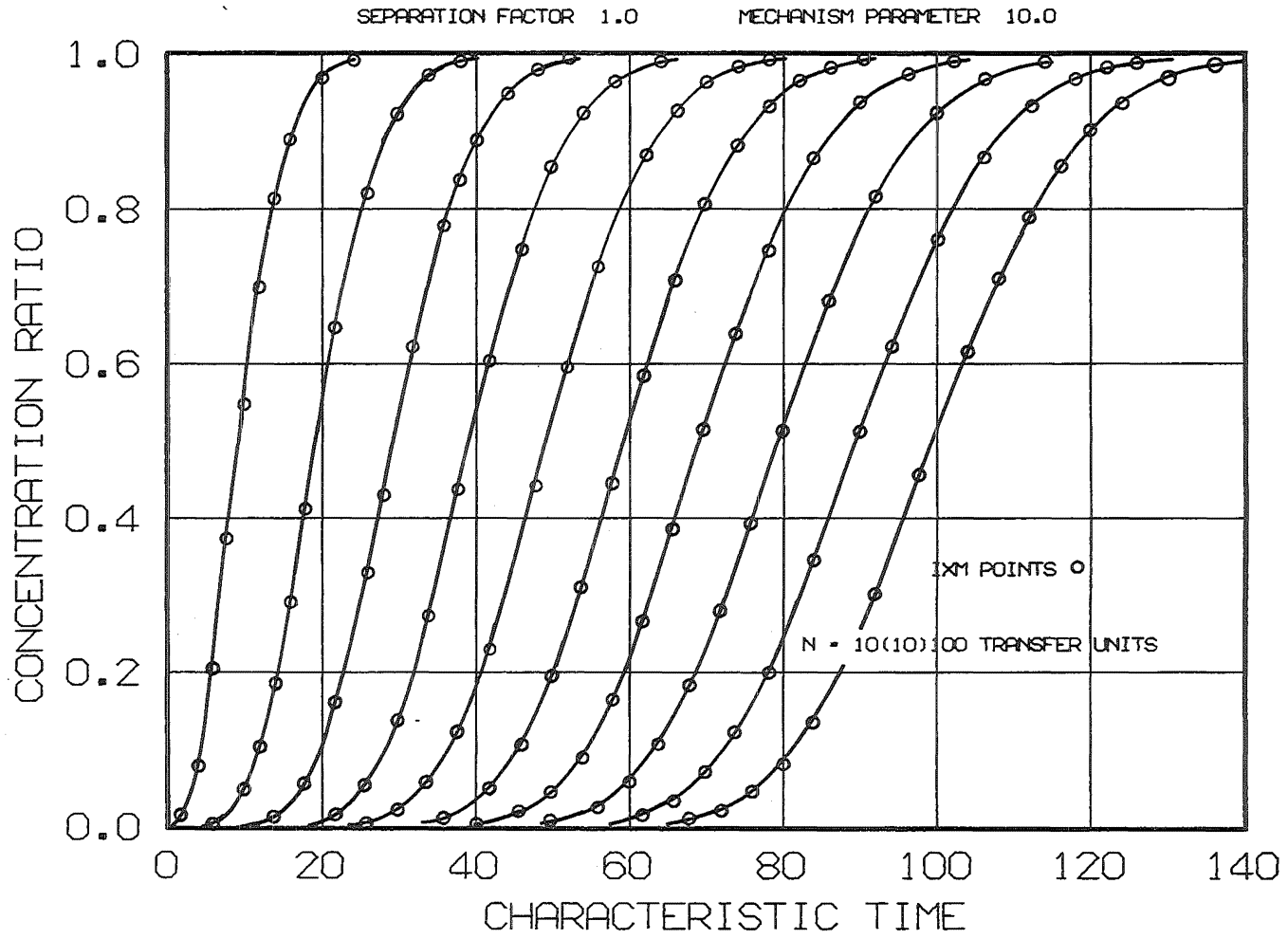
GRAPH 7-5. COMPUTED BREAKTHROUGH CURVES - IXM RESULTS COMPARED WITH IXLR CURVES.



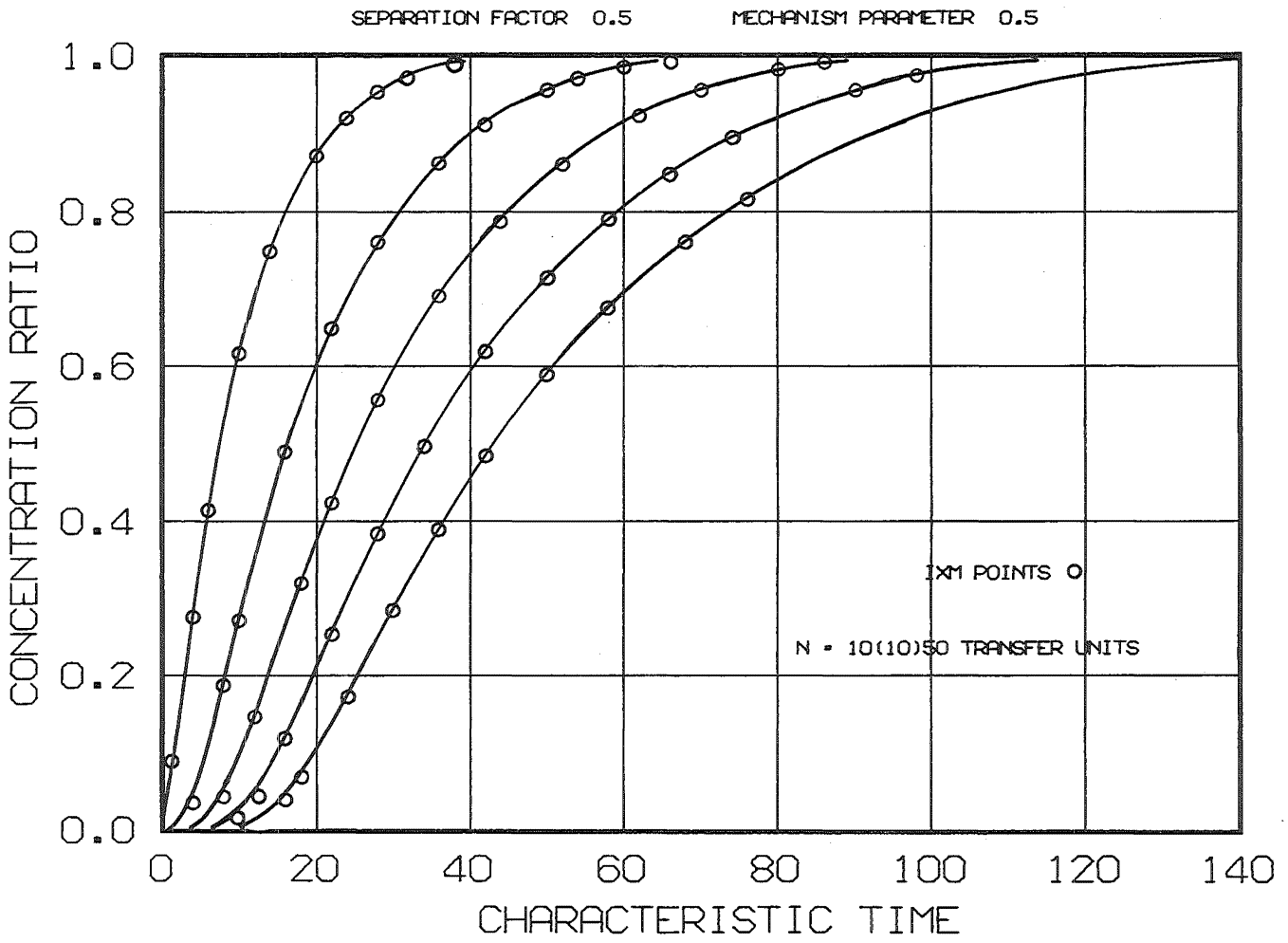
GRAPH 7-6. COMPUTED BREAKTHROUGH CURVES - IXM RESULTS COMPARED WITH IXLR CURVES.



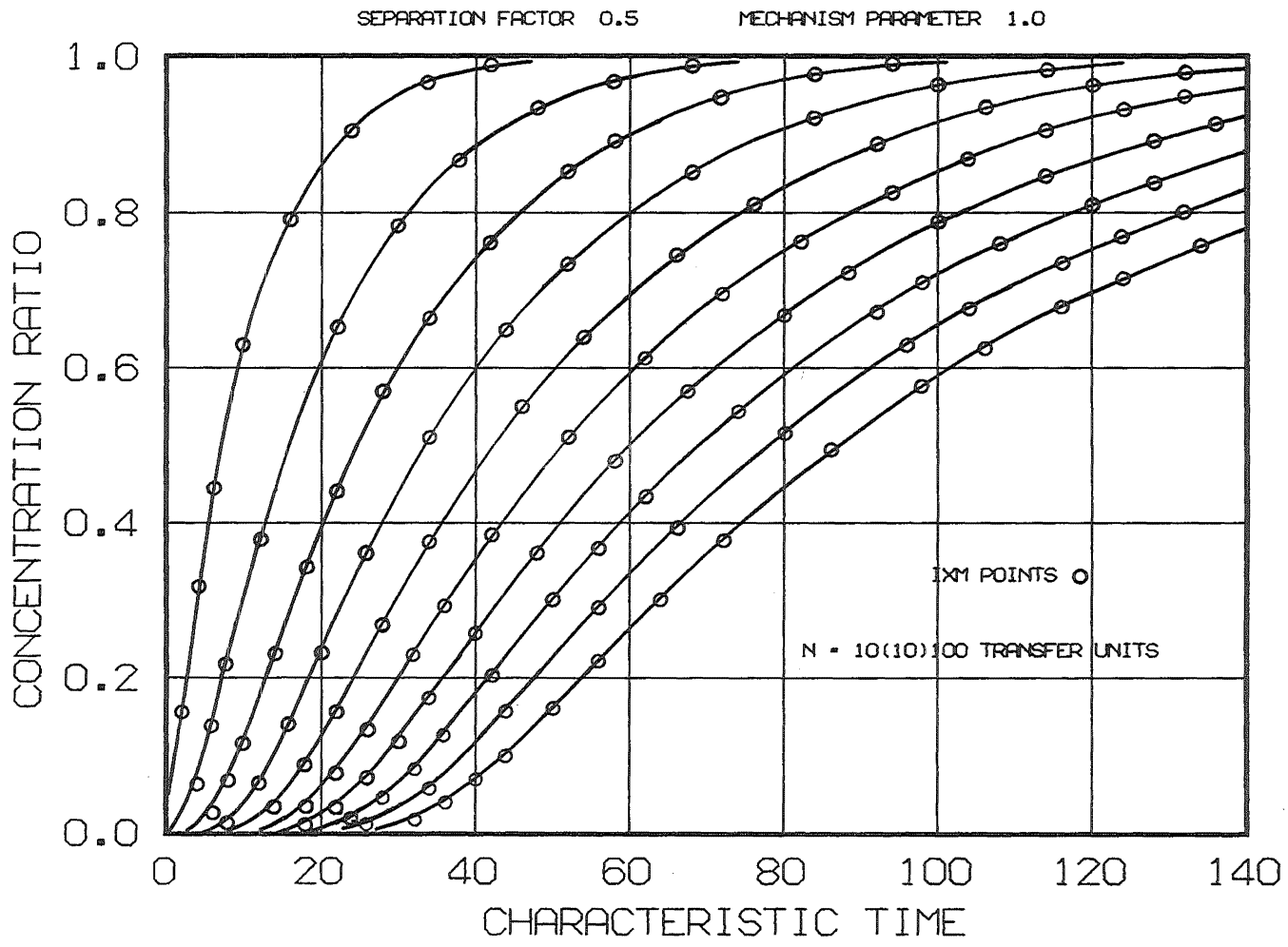
GRAPH 7-7. COMPUTED BREAKTHROUGH CURVES - IXM RESULTS COMPARED WITH IXLR CURVES.



GRAPH 7-8. COMPUTED BREAKTHROUGH CURVES - IXM RESULTS COMPARED WITH IXLR CURVES.



GRAPH 7-9. COMPUTED BREAKTHROUGH CURVES - IXM RESULTS COMPARED WITH IXLR CURVES.



GRAPH 7-10. COMPUTED BREAKTHROUGH CURVES - IXM RESULTS COMPARED WITH IXLR CURVES.

7-7 Conclusion

The IXM model for the fixed-bed ion exchange process which included a fickian particle-side diffusion equation gave results equivalent to those from the simple IXLR model of the previous chapter using a linear mass-transfer rate expression. Significant savings in computing time are possible with IXLR.

APPENDIX 7A

The Computational Equations of IXM

The solution of the film-side equations

$$\frac{\partial x}{\partial N} + \frac{\partial \bar{y}}{\partial T} = 0 \qquad (7A\text{-}1)$$

$$\frac{\partial \bar{y}}{\partial T} = \rho(x - x^*) = \text{RATE} \qquad (7A\text{-}2)$$

and the equilibrium equation

$$\frac{y^*}{1 - y^*} = K \frac{x^*}{1 - x^*} \qquad (7A\text{-}3)$$

is equivalent to that used in IXLR (Section 5-3). This appendix is concerned with the numerical solution of the particle-phase equations

$$\frac{\partial y}{\partial T} = \frac{\sigma}{15}\left(\frac{\partial^2 y}{\partial R^2} + \frac{2}{R}\frac{\partial y}{\partial R}\right) \qquad (7A\text{-}4)$$

$$\bar{y} = 3\int_0^1 R^2 y\,dR \qquad (7A\text{-}5)$$

7A-1 The Crank-Nicholson Method

Using the standard finite-difference approximations (Hausner, 1971)

$$\frac{\partial^2 y_i}{\partial R^2} = \frac{y_{i+1} - 2y_i + y_{i-1}}{2(\Delta R)^2} + Oh^3$$

$$\frac{\partial y_i}{\partial R} = \frac{y_{i+1} - y_{i-1}}{2\Delta R} + Oh^3$$

where the nomenclature is defined in Fig. 7A-1. Substituting into Eqn 7A-4:-

$$\frac{dy_i}{dT} = \frac{\sigma}{15(\Delta R)^2}\left(\frac{i \cdot y_{i+1} + (i-2) \cdot y_{i-1}}{i-1} - 2y_i\right) + Oh^3 \qquad (7A\text{-}6)$$

for i greater than 1.

At the centre of the particle,

$$i = 1, \quad \left.\frac{\partial y}{\partial R}\right|_{R=1} = 0 \quad \text{and} \quad \lim_{R\to 0} \frac{2}{R}\frac{\partial y}{\partial R} = \frac{2\partial^2 y}{\partial R^2}$$

with Eqn 7A-4 becoming at this point

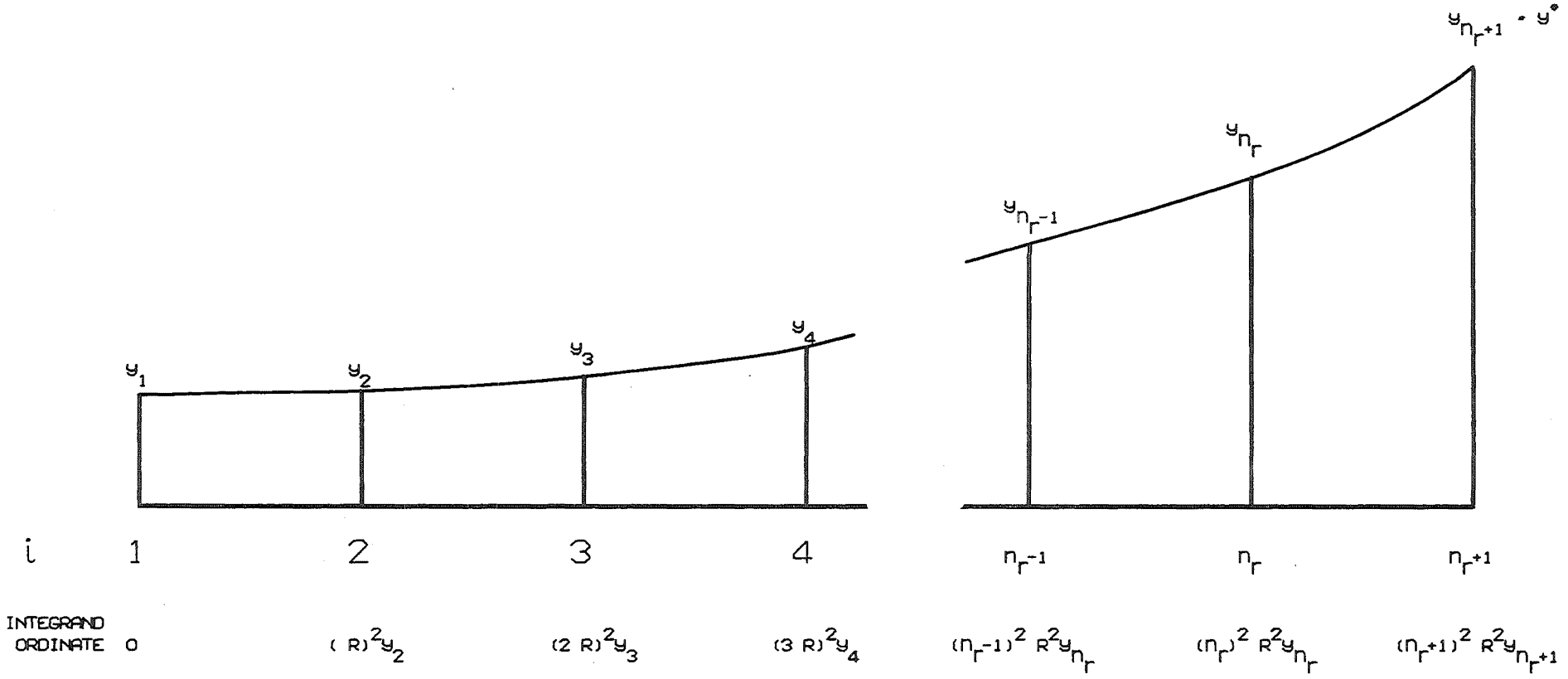


FIGURE 7A-1. PARTICLE MASS BALANCE USING SIMPSON'S RULE.

$$\left.\frac{dy}{dT}\right|_{R=0} = \frac{3\sigma}{15}\frac{\partial^2 y}{\partial R^2} = \frac{3\sigma}{15(\Delta R)^2}(y_2 - 2y_1 + y_o)$$

$$= \frac{6\sigma}{15(\Delta R)^2}(y_2 - y_1) + Oh^3 \qquad (7A\text{-}7)$$

The Crank-Nicholson method is based on the approximation

$$\frac{y_{i,T+\Delta T} - y_{i,T}}{\Delta T} = \tfrac{1}{2}\left\{\left(\frac{\partial y_i}{\partial T}\right)_{T+\Delta T} + \left(\frac{\partial y_i}{\partial T}\right)_{T}\right\} + Oh^3$$

$$\therefore \quad \left(y_i - \frac{\Delta T}{2}\frac{\partial y_i}{\partial T}\right)_{T+\Delta T} = \left(y_i + \frac{\Delta T}{2}\frac{\partial y_i}{\partial T}\right)_{T} \qquad (7A\text{-}8)$$

Substituting for the differentials at both T and T+ΔT from Eqn 7A-5 (or Eqn 7A-6 if i=1), the following equations result from the algebra:-

for i = 1

$$[-(6s + 1)y_1 + 6sy_2]_{T+\Delta T} = -[-(6s - 1)y_1 + 6sy_2]_{T} \qquad (7A\text{-}9)$$

and generally

$$\left[s\left(\frac{i-2}{i-1}\right)y_{i-1} - (2s + 1)y_i + s\frac{i}{i-1}y_{i+1}\right]_{T+\Delta T}$$

$$= -\left[\frac{s}{i-1}(iy_{i+1} + (i - 2)y_{i-1}) - (2s - 1)y_i\right]_{T} \qquad (7A\text{-}10)$$

where $s = \dfrac{\sigma\,\Delta T}{30\,(\Delta R)^2}$.

The simplification of Eqn 7A-4 with the substitution

$$p = Ry$$

giving

$$\frac{\partial p}{\partial T} = \frac{\sigma\,\partial^2 p}{\partial R^2}$$

with the elimination of the variable coefficient $\frac{2}{R}$ has not been used because it does not change the form of Eqns 7A-9, 7A-10, although it does simplify their derivation.

7A-2 The Integrated Form of the Particle Mass-Balance

The integral

$$\bar{y} = 3 \int_0^1 R^2 y dR$$

can be expressed as a summation using Simpson's rule. The integrand can be evaluated at the $n_r + 1$ equally-spaced ordinates (Fig 7A-1) to give

$$\bar{y} = (\Delta R)^3 [n_r^2 y^* + 4(y_2 + 3^2 y_4 + 5^2 y_6 \cdots (n_r - 1)^2 y_{n_r}) + 2(2^2 y_3 + 4^2 y_5 + 6^2 y_7 \cdots (n_r - 2)^2 y_{n_r - 1})] \qquad (7A\text{-}11)$$

7A-3 Calculation of Particle Concentration Profile

The solution of the $n_r + 1$ linear equations (Eqn 7A-9, 7A-10, 7A-11) in the unknowns $y_1, y_2, y_3, \cdots y_{n_r}, y^*$ at $T+\Delta T$ is best obtained (Lapidus, 1962; Rosenbrock and Storey, 1966) using Thomas' method for tridiagonal systems of equations. Table 7A-1 shows that the equations are not quite in the appropriate form (Fig 7A-2) but can readily be reduced to this form by a series of row multiplications and subtractions. Figure 7A-2 defines the Thomas method of solution.

7A-4 Calculation of RATE

With the vector y available, the RATE function can be calculated

$$y^* = y_{n_r+1}$$

$$x^* = \frac{y^*}{y^* + K(1 - y^*)}$$

$$\text{RATE} = \rho(x - x^*)$$

Figure 7A-3 is a flow-sheet of the RATE subprogram. Several entry points are used:-

(i) PRERAT - sets up the constant matrices for the Thomas method and does preliminary calculations.

(ii) RATE - calculates the RATE function for intermediate stages of Heun's method without permanently updating the concentration

$$
\begin{bmatrix}
6s+1 & 6s & & & & & & \\
0 & -(2s+1) & 2s & & & & & \\
 & & & & & & & \\
 & & & s\frac{(i-2)}{i-1} & -(2s+1) & s\frac{i}{i-1} & & \\
 & & & & & & & \\
 & & & & s\frac{(n_r-2)}{n_r-1} & -(2s+1) & s\frac{n_r}{n_r-1} & \\
0 & 4 & 8 & f(i-1)^2 & & 4(n_r-1)^2 & n_r^2 &
\end{bmatrix}
\begin{bmatrix} y_1 \\ y_2 \\ \\ y_i \\ \\ y_{n_r} \\ y_{n_r+1} \end{bmatrix}
=
\begin{bmatrix}
-[-(6s-1)y_1 + 6s\ y_2] \\
-[s(2y_3) - (2s-1)y_2] \\
 \\
-[\frac{s}{i-1}(iy_{i+1} + (i-2)y_{i-1}) - (2s-1)y_i] \\
 \\
-[\frac{s}{n_r-1}(n_r y_{n_r+1} + (n_r-2)y_{n_r-1}) \\
\qquad - (2s-1)y_{n_r}] \\
\frac{1}{(\Delta R)^3}\bar{y}
\end{bmatrix}
$$

f = 4 if i even, or 2 if odd.

TABLE 7A-1. The equations for the particle concentration profile, before reduction to the tridiagonal form.

BASIC EQUATIONS

$$\begin{bmatrix} a_1 & b_1 & & & & \\ c_2 & a_2 & b_2 & & & \\ & c_3 & a_3 & b_3 & & \\ & & \ddots & \ddots & \ddots & \\ & & & c_n & a_n \end{bmatrix} \begin{bmatrix} y_1 \\ y_2 \\ y_3 \\ \vdots \\ y_n \end{bmatrix} = \begin{bmatrix} d_1 \\ d_2 \\ d_3 \\ \vdots \\ d_n \end{bmatrix}$$

SOLUTION

$$w_1 = a_1 \qquad q_1 = \frac{b_1}{w_1}$$

FOR $i = 2$ TO n

$$w_i = a_i - c_i * q_i \qquad q_i = \frac{b_i}{w_i}$$

$$g_1 = \frac{d_1}{w_1}$$

FOR $i = 2$ TO n

$$g_i = \frac{d_i - c_i * g_{i-1}}{w_i}$$

$$y_n = g_n$$

FOR $i = n-1$ TO 1

$$y_i = g_i - q_i * y_{i+1}$$

FIGURE 7A-2. THE THOMAS METHOD OF SOLUTION FOR TRIDIAGONAL MATRICES.

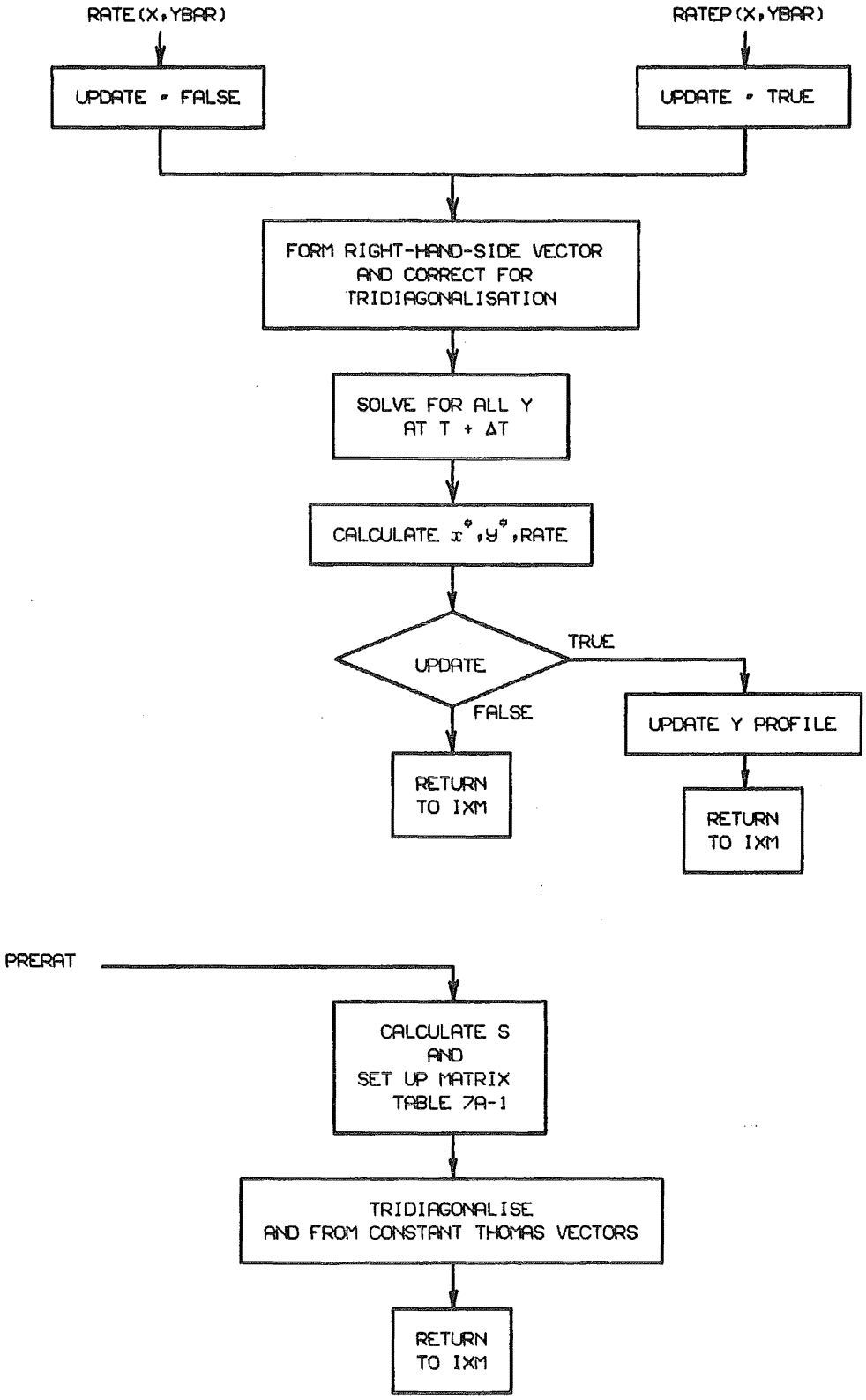


FIGURE 7A-3. FLOW SHEET FOR RATE SUBPROGRAM.

profile.

(iii) RATEP - calculates RATE and updates the profile at the close of Heun's method.

APPENDIX 7B

PROGRAM LISTING - IXM

```
C
C                                IXM
C
C     ION EXCHANGE MODEL,FICKIAN PARTICLE DIFFUSION
C
C   PURPOSE
C     TO CALCULATE FIXED-BED ION EXCHANGE COLUMN BREAKTHROUGH CURVES
C
C   USAGE
C
C     BREAKTHROUGH CURVES ARE CALCULATED FOR EACH DATA CARD READ
C
C   INPUT DATA
C
C        READ(5,100) ZETA,EK,PEND,QEND,DERP,DERQ,NINCP,NINCQ,NR
C    100 FORMAT(6E10.4,3I4)
C
C   PARAMETERS
C
C     ZETA = MECHANISM PARAMETER
C     EK = EQUILIBRIUM RATIO
C     PEND,QEND = GREATEST VALUE OF N,T REQUIRED
C     DERP,DERQ = STEP SIZE IN N,T RESPECTIVELY
C     NINCP,NINCQ = PRINT INTERVAL IN N,T IN MULTIPLES OF DERP,DERQ
C     NR=NUMBER OF SECTIONS IN RESIN RADIUS
C
C
C     THE EQUATIONS SOLVED ARE
C           DX/DN & DY/DT = 0
C                   DY/DT = R = D*(D2Y/DR2&2/R*DY/DR)
C                             = RO * (X - XSTAR)
C
C     BASIS ON SIDE WITH LESSER NUMBER OF TRANSFER UNITS
C
C   SUBPROGRAMS REQUIRED
C
C     KLOCK    TIME OF DAY IN SECONDS
C     RATE     TO CALCULATE RATE=DY/DT
C        THREE ENTRY POINTS ARE USED
C             -PRERAT  FOR INITIALISATION
C             -RATE    RESIN CONCENTRATION PROFILE NOT UPDATED
C             -RATEP   PROFILE UPDATED
C
0001          REAL*4 RHS(101)
0002          DIMENSION X(4105),Y(4105),R(4105),Q(4105),YR(101),RAD(101)
0003          COMMON DERQ,DERR,NR,NRP,SIGMA,RO,EK,YR,XSTAR,YSTAR,RHS
0004          LOGICAL PSPIT,QSPIT
C
0005        1 READ(5,100) ZETA,EK,PEND,QEND,DERP,DERQ,NINCP,NINCQ,NR
```

```
0006          100 FORMAT(6E10.4,3I4)
0007              IF(NR.EQ.0)STOP
              C   INITIALISATION TO START OF CALCULATION
0008              WRITE(6,101)
0009          101 FORMAT(1H1,45X,'ION EXCHANGE MODEL,IXM'///)
0010              IXTIME=KLOCK(3)
0011              IP=1
0012              NP=PEND/DERP+1
0013              NQ=QEND/DERQ+1
0014              NLEV=0
0015              NQP1=NQ+1
0016              NPP1=NP+1
0017              NRP=NR+1
0018              DERR=1.0/NR
0019              IRO=(NR+1)/10+1
0020              IF(IRO.EQ.0)IRO=1
0021              DO219K=1,NRP,IRO
0022              XD=K-1
0023          219 RAD(K)=XD/NR
0024              WRITE(6,102) ZETA,EK,DERP,DERQ,NR
0025          102 FORMAT(' MECHANISM PARAMETER =',T40,G12.5/' EQUILIBRIUM RATIO ='
                 3T40,G12.5,
                 1/' STEP SIZE IN N =',T40,G12.5/' STEP SIZE IN T =',T40,G12.5,
                 2/' NUMBER OF SECTIONS IN RESIN RADIUS =',T40,I3)
              C
              C   DECISION ON BASIS
0026              IF(ZETA-1.0002)50,50,51
              C
              C   PARTICLE PHASE BASIS
0027           50 RO=1.0/ZETA
0028              SIGMA=1.0
0029              WRITE(6,126)
0030          126 FORMAT(' N AND T(IE ZN) ARE BASED ON NUMBER OF PARTICLE PHASE TRAN
                 1SFER UNITS')
0031              GO TO 52
              C
              C   SOLUTION PHASE BASIS
0032           51 RO=1.0
0033              SIGMA=ZETA
0034              WRITE(6,107)
0035          107 FORMAT(' N AND T(IE ZN) ARE BASED ON NUMBER OF SOLUTION PHASE TRAN
                 1SFER UNITS')
              C
              C   INITIALISE RESIN CONCENTRATIONS
0036           52 DO129K=1,NRP
0037          129 YR(K)=0.0
0038              XD=PRERAT(0.0)
              C
              C   CALCULATION ALONG IP=1
```

```
      C
0039        X(1)=1.0
0040        Y(1)=0.0
0041        R(1)=RATE(1.0,0.0)
0042        Q(1)=0.0
0043        INIL=1
0044        DO200IQ=2,NQP1
0045        XD=IQ
0046        Q(IQ)=(XD-1.0)*DERQ
0047        X(IQ)=1.0
      C
      C     CHECK THAT Y NOT 1.0
0048        IF(Y(IQ-1).LE.0.9999) GO TO 17
0049        Y(IQ)=1.0
0050        R(IQ)=0.0
0051        GO TO 200
      C
      C     RUNGE KUTTA PROCEDURE TO GET Y(IQ), NOTE X(IQ)=1.0
0052     17 YO=Y(IQ-1)
0053        RKO=DERQ*R(IQ-1)
0054        XD=YO+.5*RKO
0055        RK1=DERQ*RATE(1.0,XD)
0056        XD=YO+RK1*.5
0057        RK2=DERQ*RATE(1.0,XD)
0058        XD=YO+RK2
0059        RK3=DERQ*RATE(1.0,XD)
0060        Y1=YO+(RKO+2.0*(RK1+RK2)+RK3)/6.0
0061        Y(IQ)=Y1
0062        R(IQ)=RATEP(1.0,Y1)
0063        ISAT=IQ
0064    200 CONTINUE
      C
      C     NOW SUCCESSIVE INCREMENTATION DOWN COLUMN
      C
0065        DO204IP=2,NPP1
      C
      C     INITIALISE RESIN CONCENTRATIONS
0066        DO127K=1,NRP
0067    127 YR(K)=0.0
      C     IS PRINTOUT OF BREAKTHROUGH CURVES REQUIRED AT THIS LEVEL OF P
0068     13 NLEV=NLEV+1
0069        IF(NLEV.LT.NINCP) GO TO 74
0070        P=IP-1
0071        P=P*DERP
0072        WRITE(6,103) P
0073    103 FORMAT(1H1,'NUMBER OF TRANSFER UNITS =',G12.5/)
0074        WRITE(6,104)
0075    104 FORMAT(6X,'T',7X,'Z',7X,'X',7X,'Y',5X,'XSTAR',3X,'YSTAR',14X,
           1'RESIN CONCENTRATION AT SPECIFIED FRACTION OF RADIUS')
```

```
0076              NLEV=0
0077              WRITE(6,117)(RAD(K),K=1,NR,IRO)
0078            117 FORMAT(49X,10F8.3/)
0079              PSPIT=.TRUE.
0080              GO TO 81
0081             74 PSPIT=.FALSE.
0082             81 IF(INIL.NE.1) GO TO 12
                 C
                 C     INIL=1, CALCULATION OF X(1), NOTE Y(1)=0.0, USING RUNGE KUTTA
0083              XO=X(1)
0084              RKO=-DERP*R(1)
0085              XD=XO+RKO*.5
0086              RK1=-DERP*RATE(XD,0.0)
0087              XD=XO+RK1*.5
0088              RK2=-DERP*RATE(XD,0.0)
0089              XD=XO+RK2
0090              RK3=-DERP*RATE(XD,0.0)
0091              X1=XO+(RKO+RK3+2.0*(RK1+RK2))/6.0
0092              X(1)=X1
0093              R(1)=RATEP(X1,0.0)
0094              JSAT=2
0095              GO TO 6
                 C
                 C     CALCULATION OF OTHER X,Y AT THIS LEVEL OF P
0096             12 JSAT=INIL
0097              6 IGO=JSAT-NINCQ*((JSAT-1)/NINCQ)-1
0098                DO201IQ=JSAT,NQP1
0099                IF(IGO.GE.NINCQ)GO TO 78
                 C
                 C     NO PRINT OUT
0100                IGO=IGO+1
0101                QSPIT=.FALSE.
0102                GOTO 71
                 C
                 C      PRINTOUT REQUIRED
0103             78 IGO=1
0104                QSPIT=.TRUE.
                 C     FETCH THE REQUIRED SUBSCRIPTED VARIABLES
0105             71 R2=R(IQ)
0106                X2=X(IQ)
0107                Y1=Y(IQ-1)
0108                R1=R(IQ-1)
                 C
                 C     CALCULATE FIRST ESTIMATES OF X,Y AT NEW POINT
0109                XD=X2-R2*DERP
0110                YD=Y1+R1*DERQ
                 C
                 C     CHECK THAT X,Y NOT LESS THAN .0001
0111                IF(XD+YD.GT.0.0001) GO TO 21
```

```
                C     COLUMN STILL EMPTY, NORMAL RETURN
0112                  X(IQ)=0.0
0113                  Y(IQ)=0.0
0114                  R(IQ)=0.0
0115                  INIL=IQ
0116                  GO TO 77
                C
                C     CHECK THAT X,Y NOT GREATER THAN .9999
0117             21   IF(XD+YD.LT.1.9999) GO TO 22
                C     COLUMN SATURATED, BRANCH OUT OF LOOP
0118                  X(IQ)=1.0
0119                  Y(IQ)=1.0
0120                  R(IQ)=0.0
0121                  ISAT=IQ
                C
                C    RESIN AND SOLUTION SATURATED
0122                  GO TO 204
                C
                C     CALCULATION OF SECOND ESTIMATES OF X,Y AT THIS POINT
0123             22   RD=RATE(XD,YD)
0124                  XDD=X2-RD*DERP
0125                  YDD=Y1+RD*DERQ
                C
                C     CALCULATION OF FINAL VALUES OF X,Y AT THIS POINT
0126                  X2=0.5*(XD+XDD)
0127                  Y2=0.5*(YD+YDD)
0128                  R2=RATEP(X2,Y2)
                C
                C     CHECK X IN ACCEPTABLE RANGE
0129                  IF(X2.GT.-0.1000.AND.X2.LT.1.1000) GO TO 33
                C     X OUTSIDE RANGE
0130                  WRITE(6,108)IP,IQ
0131             108  FORMAT(' SOLUTION CONCENTRATION NOT IN ACCEPTABLE RANGE'
                    1' IP='I4,3X'IQ='I4,//)
0132                  DO240K=1,NQP1,2
0133                  IF(K.GT.50)GOTO59
0134                  L=K+1
0135             240  WRITE(6,140)K,X(K),Y(K),R(K),X(L),Y(L),R(L)
0136             140  FORMAT(I4,6G20.6)
0137                  WRITE(6,141)(RHS(K),K=1,NRP)
0138             141  FORMAT(6G20.6)
0139                  GO TO 59
0140              33  X(IQ)=X2
0141                  Y(IQ)=Y2
0142                  R(IQ)=R2
0143              77  IF(PSPIT.AND.QSPIT)GO TO 27
0144                  GO TO 201
0145              27  Z=Q(IQ)/P
0146                  WRITE(6,105)Q(IQ),Z,X2,Y2,XSTAR,YSTAR,(YR(K),K=1,NR,IRO)
```

```
0147          105 FORMAT(1X,F8.2,5F8.5,10F8.4)
0148          201 CONTINUE
0149          204 CONTINUE
0150              IXTIME=KLOCK(3)-IXTIME
0151              WRITE(6,133) IXTIME
0152          133 FORMAT(////G10.4)
0153           59 GO TO 1
0154              END
```

```
0001            FUNCTION RATE(X,YBAR)
                C
                C   PURPOSE
                C
                C     THIS SUBPROGRAM IS TO CALCULATE RATE=DYBAR/DT=-DX/DN=RO*(X-XSTAR)
                C     USING THE PARTICLE SIDE MASS BALANCE
                C     YBAR=3*INTEGRAL R*R*Y*DR
                C     AND THE EQUATION FOR DIFFUSION INTO A SPHERE
                C     DY/DT=SIGMA*(D2Y/DR2&2/R*DY/DR)
                C
                C
                C   USAGE
                C
                C     R=RATE(X,YBAR)
                C
                C   PARAMETERS
                C
                C     R       THE CALCULATED RATE
                C     X       SOLUTION CONCENTRATION RATIO
                C     Y       AVERAGE PARTICLE CONCENTRATION RATIO
0002            DIMENSION Y(101)
0003            REAL*4 FACT(101),RHS(101),CTOM(101),GTOM(101),WTOM(101),
                1QTOM(101),ELLFT(101),ELCNTR(101),ELRHT(101),ELBOT(101),
                2RHSNRP,FAC1
0004            COMMON DERT,DERR,NR,NRP,SIGMA,RO,EK,Y,XSTAR,YSTAR,RHS
0005            EQUIVALENCE(WTOM(1),ELCNTR(1)),(QTOM(1),ELRHT(1)),(CTOM(1),ELLFT(1
                1)),(ELBOT(1),RHS(1))
0006            ISWCH=-1
0007            GO TO 1
                C
                C     THIS ENTRY POINT WILL UPOATE THE RESIN CONCENTRATION PROFILE
                C
0008            ENTRY RATEP(X,YBAR)
0009            ISWCH=+1
                C
                C     FORM THE RIGHT HAND VECTOR
                C     NOTE THAT THE ENTRY PRERATE WILL HAVE BEEN USED
                C
0010          1 RHS(1)=-((TWOS*3.0-1.0)*Y(1)-3.0*TWOS*Y(2))
0011            DO200IROW=2,NR
0012            IROWP=IROW+1
0013            IROWM=IROW-1
0014            RIROWM=1.0/IROWM
0015          200 RHS(IROW)=-(S*RIROWM*((IROWM-1)*Y(IROWM)+IROW*Y(IROWP))-TWOSM*Y(IR
                10W))
0016            RHSNRP=YBAR/(DERR*DERR*DERR)
0017            RHS(NRP)=RHSNRP
                C                                       )PRN,1=WORI,)WORI(SHR( )803,6(ETIRW
0018          308 FORMAT(//, 10G13.5)
```

```
C
C     NOW CORRECT RHS VECTOR FOR MANIPULATIONS TO GET IN TRIDIAGONAL
C     FORM
C
C     FOR ROWS 3 TO NR,MULTIPLY RHS(NRP) BY FACT(IROW)
C        THEN SUBTRACT RHS(IROW)FROM IT
C
0019        DO201IROW=3,NR
0020      201 RHSNRP=RHSNRP*FACT(IROW)-RHS(IROW)
0021        RHS(NRP)=RHSNRP
C
C     THE RHS VECTOR IS NOW EQUAL TO THE DTOM VECTOR
C     THE GTOM CAN NOW BE EVALUATED
0022        GTOM(1)=RHS(1)/WTOM(1)
0023        DO202IROW=2,NRP
0024      202 GTOM(IROW)=(RHS(IROW)-CTOM(IROW)*GTOM(IROW-1))/WTOM(IROW)
C                                          )PRN,1=WORI,)WORI(MOTG( )803,6(ETIRW
C                                           )PRN,1=WORI,)WORI(SHR( )803,6(ETIRW
0025        YSTAR=GTOM(NRP)
0026        XSTAR=YSTAR/(YSTAR+EK*(1.0-YSTAR))
0027        RATE=RO*(X-XSTAR)
C                                                              )YXEMAN,6(ETIRW
C                                             ETAR,RATSY,RATSX/YXEMAN/TSILEMAN
0028        IF(ISWCH)3,3,4
C
C     DO NOT UPDATE PROFILE
C
0029        3 RETURN
C
C     THE NEW Y VECTOR CAN BE EVALUATED
C
0030        4 Y(NRP)=YSTAR
0031        DO203II=1,NR
0032        IROW=NRP-II
0033      203 Y(IROW)=GTOM(IROW)-QTOM(IROW)*Y(IROW+1)
C                                          )PRN,1=WORI,)WORI(Y( )803,6(ETIRW
C                                  )//'ELIFORP NOITARTNECNOC NISER',X05(TAMROF 903
C                                                              )903,6(ETIRW
0034        RATEP=RATE
0035        RETURN
C
C
C     ****************************************************************
C
C
0036        ENTRY PRERAT(XXX)
C
C     THIS ENTRY PERFORMS THE PRELIMINARY CALCULATIONS FOR RATE
C
```

```
0037              S=DERT*SIGMA/(30.0*DERR*DERR)
                C
                C     SET UP THE MATRIX EL
                C
0038              TWOS=S+S
0039              TWOSM=TWOS-1.0
0040              TWOSP=-(TWOS+1.0)
0041              ELLFT(1)=0.0
0042              ELCNTR(1)=3.0*TWOS+1.0
0043              ELRHT(1)=-3.0*TWOS
0044              DO251IROW=2,NR
0045              IROWP=IROW+1
0046              IROWM=IROW-1
0047              RIROWM=1.0/IROWM
0048              ELLFT(IROW)=S*(IROWM-1.0)*RIROWM
0049              ELCNTR(IROW)=TWOSP
0050            251 ELRHT(IROW)=S*IROW*RIROWM
                C
                C     FOR THE BOTTOM ROW,IROW=NR&1
0051              ELBOT(1)=0.0
0052              WT=4.0
0053              DO252ICOL=2,NR
0054              ICOLM=ICOL-1
0055              ELBOT(ICOL)=ICOLM*ICOLM*WT
0056              IF(WT-3.0)22,22,24
0057             22 WT=4.0
0058                GO TO 252
0059             24 WT=2.0
0060            252 CONTINUE
0061              ELBOT(NRP)=NR*NR
0062              WRITE(6,300)                                                    C
0063              WRITE(6,303)                                                    C
0064            300 FORMAT(26X,'BASIC MATRIX'//)                                  C
0065            303 FORMAT('  IROW'3X'ELLFT'9X'ELCNTR'9X'ELRHT'9X'ELBOT'/)       C
0066              DO 302 IROW=1,NRP                                               C
0067              WRITE(6,301) IROW,ELLFT(IROW),ELCNTR(IROW),ELRHT(IROW),ELBOT(IROW)  C
0068            301 FORMAT(I6,4G14.7)                                             C
0069            302 CONTINUE                                                      C
                C
                C     THE MATRIX EL MUST BE PUT IN THE TRIDIAGONAL FORM
                C     FOR EACH ROW,FROM ROW 3 TO ROW NR, MULTIPLY WHAT REMAINS OF THE
                C        BOTTOM ROW BY THE RATIO OF THE FIRST ELEMENT OF THAT ROW
                C        TO THAT IN THE BOTTOM ROW (THIS IS THE RATIO FACT)
0070              FACT(1)=1.0
0071              FACT(2)=1.0
0072              DO253IROW=3,NR
0073              IROWP=IROW+1
0074              IROWM=IROW-1
0075              FAC1=ELLFT(IROW)/ELBOT(IROWM)
```

```
0076                FACT(IROW)=FAC1
0077                DO255ICOL=IROWM,NRP
0078              255 ELBOT(ICOL)=ELBOT(ICOL)*FAC1
                  C
                  C     NOW SUBTRACT ROW IROW FROM BOTTOM ROW
                  C
0079                ELBOT(IROWM)=0.0
0080                ELBOT(IROW)=ELBOT(IROW)-ELCNTR(IROW)
0081              253 ELBOT(IROWP)=ELBOT(IROWP)-ELRHT(IROW)
0082                ELLFT(NRP)=ELBOT(NR)
0083                ELCNTR(NRP)=ELBOT(NRP)
0084                WRITE(6,304)                                                    C
0085              304 FORMAT(//26X,'THOMAS FORM'//)                                 C
0086                WRITE(6,303)                                                    C
0087                DO 305 IROW=1,NRP                                               C
0088              305 WRITE(6,301) IROW,ELLFT(IROW),ELCNTR(IROW),ELRHT(IROW),ELBOT(IROW)  C
                  C
                  C     THE MATRIX EL IS NOW TRIPLE DIAGONAL
                  C     THE VECTORS WTOM,QTOM,CTOM WHICH ARE REQUIRED
                  C     FOR THE THOMAS METHOD OF INVERSION CAN BE
                  C     CALCULATED AND USED AT ALL POINTS
0089                WTOM(1)=ELCNTR(1)
0090                DO254IROW=2,NRP
0091                IROWM=IROW-1
0092                QTOM(IROWM)=ELRHT(IROWM)/WTOM(IROWM)
0093              254 WTOM(IROW)=ELCNTR(IROW)-ELLFT(IROW)*QTOM(IROWM)
0094                WTOM(NRP)=ELBOT(NRP)-ELBOT(NR)*QTOM(NR)
0095                WRITE(6,306)                                                    C
0096              306 FORMAT('  IROW'4X'QTOM'10X'WTOM'10X'CTOM'/)                   C
0097                DO 307 IROW=1,NRP                                               C
0098              307 WRITE(6,301) IROW,QTOM(IROW),WTOM(IROW),CTOM(IROW)            C
0099                PRERAT=4.0
0100                RETURN
0101                END
```

MECHANISM PARAMETER = 1.0000
EQUILIBRIUM RATIO = 1.0000
STEP SIZE IN N = 0.12500
STEP SIZE IN T = 0.25000
NUMBER OF SECTIONS IN RESIN RADIUS = 4
N AND T(IE ZN) ARE BASED ON NUMBER OF PARTICLE PHASE TRANSFER UNITS

BASIC MATRIX

IROW	ELLFT	ELCNTR	ELRHT	ELBOT
1	0.0	1.799999	-0.8000000	0.0
2	0.0	-1.266666	0.2666667	4.000000
3	0.6666666E-01	-1.266666	0.2000000	8.000000
4	0.8888882E-01	-1.266666	0.1777777	36.00000
5	0.0	0.0	0.0	16.00000

THOMAS FORM

IROW	ELLFT	ELCNTR	ELRHT	ELBOT
1	0.0	1.799999	-0.8000000	0.0
2	0.0	-1.266666	0.2666667	0.0
3	0.6666666E-01	-1.266666	0.2000000	0.0
4	0.8888882E-01	-1.266666	0.1777777	1.292063
5	1.292063	-0.1608465	0.0	-0.1608465

IROW	QTOM	WTOM	CTOM
1	-0.4444446	1.799999	0.0
2	-0.2105263	-1.266666	0.0
3	-0.1596639	-1.252631	0.6666666E-01
4	-0.1419412	-1.252474	0.8888882E-01
5	0.0	0.2255052E-01	1.292063

NUMBER OF TRANSFER UNITS = 10.000

T	Z	X	Y	XSTAR	YSTAR	RESIN CONCENTRATION AT SPECIFIED FRACTION OF RADIUS			
						0.0	0.250	0.500	0.750
1.00	0.10000	0.01361	0.00296	0.00692	0.00692	0.0001	0.0002	0.0006	0.0020
2.00	0.20000	0.05110	0.01701	0.03158	0.03158	0.0026	0.0035	0.0066	0.0144
3.00	0.30000	0.10294	0.04396	0.07072	0.07072	0.0127	0.0151	0.0231	0.0399
4.00	0.40000	0.16456	0.08280	0.12112	0.12112	0.0339	0.0381	0.0517	0.0777
5.00	0.50000	0.23239	0.13167	0.17984	0.17984	0.0667	0.0727	0.0914	0.1258
6.00	0.60000	0.30336	0.18826	0.24410	0.24410	0.1101	0.1176	0.1408	0.1819
7.00	0.70000	0.37485	0.25016	0.31131	0.31131	0.1621	0.1708	0.1974	0.2435
8.00	0.80000	0.44479	0.31502	0.37920	0.37920	0.2207	0.2302	0.2591	0.3084
9.00	0.90000	0.51156	0.38077	0.44590	0.44590	0.2834	0.2934	0.3235	0.3743
10.00	1.00000	0.57404	0.44562	0.50994	0.50994	0.3480	0.3582	0.3887	0.4394
11.00	1.10000	0.63152	0.50814	0.57025	0.57025	0.4128	0.4228	0.4528	0.5023
12.00	1.20000	0.68362	0.56729	0.62610	0.62610	0.4760	0.4857	0.5146	0.5619
13.00	1.30000	0.73023	0.62231	0.67708	0.67708	0.5365	0.5457	0.5730	0.6174
14.00	1.40000	0.77146	0.67275	0.72302	0.72302	0.5934	0.6020	0.6273	0.6684
15.00	1.50000	0.80755	0.71840	0.76394	0.76394	0.6460	0.6539	0.6771	0.7145
16.00	1.60000	0.83886	0.75924	0.80002	0.80002	0.6940	0.7011	0.7222	0.7558
17.00	1.70000	0.86579	0.79540	0.83154	0.83154	0.7372	0.7436	0.7624	0.7924
18.00	1.80000	0.88877	0.82712	0.85885	0.85885	0.7758	0.7814	0.7981	0.8245
19.00	1.90000	0.90825	0.85471	0.88233	0.88233	0.8098	0.8148	0.8294	0.8525
20.00	2.00000	0.92465	0.87851	0.90236	0.90236	0.8396	0.8439	0.8566	0.8766
21.00	2.10000	0.93838	0.89891	0.91934	0.91934	0.8654	0.8691	0.8801	0.8973
22.00	2.20000	0.94981	0.91625	0.93365	0.93365	0.8876	0.8908	0.9002	0.9149
23.00	2.30000	0.95928	0.93092	0.94566	0.94566	0.9066	0.9093	0.9173	0.9298
24.00	2.40000	0.96707	0.94325	0.95568	0.95568	0.9227	0.9250	0.9318	0.9423
25.00	2.50000	0.97347	0.95356	0.96393	0.96393	0.9363	0.9383	0.9440	0.9528
26.00	2.60000	0.97868	0.96214	0.97078	0.97078	0.9478	0.9494	0.9541	0.9615
27.00	2.70000	0.98292	0.96925	0.97636	0.97636	0.9573	0.9586	0.9626	0.9687
28.00	2.80000	0.98637	0.97509	0.98097	0.98097	0.9652	0.9663	0.9696	0.9747
29.00	2.90000	0.98914	0.97990	0.98478	0.98478	0.9718	0.9727	0.9754	0.9796
30.00	3.00000	0.99139	0.98382	0.98778	0.98778	0.9772	0.9779	0.9801	0.9835
31.00	3.10000	0.99317	0.98702	0.99023	0.99023	0.9816	0.9822	0.9840	0.9868
32.00	3.20000	0.99461	0.98962	0.99222	0.99222	0.9852	0.9857	0.9872	0.9894
33.00	3.30000	0.99576	0.99172	0.99383	0.99383	0.9881	0.9885	0.9897	0.9916
34.00	3.40000	0.99667	0.99340	0.99514	0.99514	0.9905	0.9908	0.9918	0.9933
35.00	3.50000	0.99739	0.99477	0.99615	0.99615	0.9924	0.9927	0.9935	0.9947
36.00	3.60000	0.99795	0.99586	0.99696	0.99696	0.9940	0.9942	0.9948	0.9958
37.00	3.70000	0.99840	0.99673	0.99763	0.99763	0.9952	0.9954	0.9959	0.9967
38.00	3.80000	0.99876	0.99742	0.99810	0.99810	0.9962	0.9964	0.9968	0.9974
39.00	3.90000	0.99904	0.99797	0.99852	0.99852	0.9970	0.9971	0.9975	0.9979
40.00	4.00000	0.99926	0.99841	0.99890	0.99890	0.9977	0.9977	0.9980	0.9984
41.00	4.10000	0.99943	0.99876	0.99911	0.99911	0.9982	0.9982	0.9984	0.9987
42.00	4.20000	0.99957	0.99903	0.99933	0.99933	0.9986	0.9986	0.9988	0.9990
43.00	4.30000	0.99967	0.99925	0.99945	0.99945	0.9989	0.9989	0.9991	0.9992
44.00	4.40000	0.99976	0.99942	0.99958	0.99958	0.9991	0.9992	0.9993	0.9994
45.00	4.50000	0.99983	0.99955	0.99971	0.99971	0.9993	0.9994	0.9994	0.9996
46.00	4.60000	0.99988	0.99967	0.99979	0.99979	0.9995	0.9995	0.9996	0.9997
47.00	4.70000	0.99992	0.99975	0.99988	0.99988	0.9996	0.9996	0.9997	0.9998
48.00	4.80000	0.99996	0.99981	0.99992	0.99992	0.9997	0.9997	0.9998	0.9998
49.00	4.90000	0.99998	0.99987	0.99996	0.99996	0.9998	0.9998	0.9998	0.9999

NUMBER OF TRANSFER UNITS = 50.000

T	Z	X	Y	XSTAR	YSTAR	RESIN CONCENTRATION AT SPECIFIED FRACTION OF RADIUS			
						0.0	0.250	0.500	0.750
14.00	0.28000	0.00023	0.00006	0.00013	0.00013	0.0000	0.0000	0.0000	0.0000
15.00	0.30000	0.00045	0.00019	0.00031	0.00031	0.0000	0.0001	0.0001	0.0002
16.00	0.32000	0.00080	0.00038	0.00057	0.00057	0.0001	0.0002	0.0002	0.0003
17.00	0.34000	0.00132	0.00067	0.00097	0.00097	0.0003	0.0003	0.0004	0.0006
18.00	0.36000	0.00206	0.00111	0.00155	0.00155	0.0006	0.0006	0.0008	0.0010
19.00	0.38000	0.00310	0.00174	0.00237	0.00237	0.0009	0.0010	0.0012	0.0017
20.00	0.40000	0.00452	0.00263	0.00351	0.00351	0.0015	0.0016	0.0019	0.0025
21.00	0.42000	0.00641	0.00384	0.00505	0.00505	0.0023	0.0024	0.0028	0.0037
22.00	0.44000	0.00888	0.00545	0.00707	0.00707	0.0033	0.0035	0.0041	0.0052
23.00	0.46000	0.01202	0.00756	0.00967	0.00967	0.0048	0.0050	0.0058	0.0073
24.00	0.48000	0.01595	0.01027	0.01296	0.01296	0.0066	0.0070	0.0080	0.0099
25.00	0.50000	0.02078	0.01367	0.01706	0.01706	0.0091	0.0095	0.0108	0.0133
26.00	0.52000	0.02664	0.01787	0.02206	0.02206	0.0122	0.0127	0.0144	0.0174
27.00	0.54000	0.03362	0.02299	0.02809	0.02809	0.0160	0.0167	0.0187	0.0224
28.00	0.56000	0.04183	0.02913	0.03524	0.03524	0.0207	0.0215	0.0240	0.0284
29.00	0.58000	0.05136	0.03638	0.04361	0.04361	0.0263	0.0273	0.0303	0.0355
30.00	0.60000	0.06230	0.04486	0.05329	0.05329	0.0331	0.0342	0.0377	0.0439
31.00	0.62000	0.07469	0.05463	0.06435	0.06435	0.0409	0.0423	0.0464	0.0535
32.00	0.64000	0.08859	0.06577	0.07686	0.07686	0.0501	0.0516	0.0563	0.0645
33.00	0.66000	0.10402	0.07834	0.09084	0.09084	0.0606	0.0623	0.0676	0.0769
34.00	0.68000	0.12098	0.09237	0.10632	0.10632	0.0724	0.0744	0.0804	0.0908
35.00	0.70000	0.13945	0.10788	0.12331	0.12331	0.0857	0.0879	0.0946	0.1062
36.00	0.72000	0.15940	0.12488	0.14178	0.14178	0.1005	0.1029	0.1103	0.1230
37.00	0.74000	0.18075	0.14333	0.16168	0.16168	0.1168	0.1194	0.1275	0.1414
38.00	0.76000	0.20344	0.16321	0.18297	0.18297	0.1345	0.1374	0.1461	0.1611
39.00	0.78000	0.22735	0.18445	0.20556	0.20556	0.1536	0.1567	0.1661	0.1822
40.00	0.80000	0.25239	0.20696	0.22935	0.22935	0.1742	0.1775	0.1875	0.2046
41.00	0.82000	0.27841	0.23066	0.25424	0.25424	0.1960	0.1995	0.2101	0.2282
42.00	0.84000	0.30529	0.25544	0.28009	0.28009	0.2191	0.2228	0.2340	0.2529
43.00	0.86000	0.33286	0.28117	0.30676	0.30676	0.2433	0.2471	0.2588	0.2785
44.00	0.88000	0.36098	0.30772	0.33412	0.33412	0.2685	0.2725	0.2846	0.3050
45.00	0.90000	0.38950	0.33494	0.36202	0.36202	0.2946	0.2987	0.3112	0.3322
46.00	0.92000	0.41824	0.36269	0.39030	0.39030	0.3214	0.3257	0.3385	0.3599
47.00	0.94000	0.44707	0.39083	0.41882	0.41882	0.3489	0.3532	0.3662	0.3880
48.00	0.96000	0.47582	0.41918	0.44741	0.44741	0.3768	0.3812	0.3943	0.4164
49.00	0.98000	0.50436	0.44762	0.47593	0.47593	0.4050	0.4094	0.4227	0.4448
50.00	1.00000	0.53255	0.47600	0.50424	0.50424	0.4333	0.4378	0.4511	0.4732
51.00	1.02000	0.56026	0.50416	0.53220	0.53220	0.4617	0.4661	0.4794	0.5014
52.00	1.04000	0.58737	0.53200	0.55971	0.55971	0.4899	0.4943	0.5075	0.5293
53.00	1.06000	0.61379	0.55937	0.58663	0.58663	0.5179	0.5222	0.5352	0.5568
54.00	1.08000	0.63942	0.58618	0.61288	0.61288	0.5454	0.5497	0.5625	0.5836
55.00	1.10000	0.66418	0.61232	0.63835	0.63835	0.5725	0.5767	0.5892	0.6098
56.00	1.12000	0.68800	0.63769	0.66297	0.66297	0.5990	0.6030	0.6152	0.6353
57.00	1.14000	0.71084	0.66223	0.68667	0.68667	0.6247	0.6286	0.6405	0.6599
58.00	1.16000	0.73265	0.68586	0.70941	0.70941	0.6496	0.6534	0.6649	0.6837
59.00	1.18000	0.75340	0.70854	0.73113	0.73113	0.6737	0.6774	0.6884	0.7064
60.00	1.20000	0.77306	0.73021	0.75182	0.75182	0.6968	0.7004	0.7109	0.7282
61.00	1.22000	0.79165	0.75086	0.77144	0.77144	0.7190	0.7224	0.7325	0.7490
62.00	1.24000	0.80914	0.77045	0.78999	0.78999	0.7401	0.7434	0.7530	0.7687
63.00	1.26000	0.82556	0.78899	0.80747	0.80747	0.7603	0.7633	0.7724	0.7873
64.00	1.28000	0.84092	0.80647	0.82390	0.82390	0.7793	0.7822	0.7908	0.8049
65.00	1.30000	0.85525	0.82289	0.83927	0.83927	0.7973	0.8001	0.8082	0.8214
66.00	1.32000	0.86857	0.83827	0.85362	0.85362	0.8143	0.8169	0.8245	0.8369
67.00	1.34000	0.88092	0.85264	0.86697	0.86697	0.8302	0.8326	0.8398	0.8514
68.00	1.36000	0.89233	0.86601	0.87937	0.87937	0.8451	0.8473	0.8540	0.8648
69.00	1.38000	0.90285	0.87843	0.89083	0.89083	0.8590	0.8611	0.8673	0.8773
70.00	1.40000	0.91253	0.88993	0.90142	0.90142	0.8719	0.8738	0.8796	0.8889
71.00	1.42000	0.92139	0.90055	0.91115	0.91115	0.8839	0.8857	0.8910	0.8996
72.00	1.44000	0.92949	0.91032	0.92007	0.92007	0.8949	0.8966	0.9015	0.9095
73.00	1.46000	0.93689	0.91928	0.92824	0.92824	0.9051	0.9067	0.9112	0.9185
74.00	1.48000	0.94363	0.92750	0.93572	0.93572	0.9145	0.9159	0.9201	0.9268
75.00	1.50000	0.94973	0.93500	0.94249	0.94249	0.9231	0.9244	0.9282	0.9344
76.00	1.52000	0.95525	0.94184	0.94866	0.94866	0.9310	0.9322	0.9357	0.9413
77.00	1.54000	0.96023	0.94804	0.95424	0.95424	0.9382	0.9393	0.9424	0.9475
78.00	1.56000	0.96472	0.95369	0.95932	0.95932	0.9447	0.9457	0.9486	0.9532
79.00	1.58000	0.96876	0.95879	0.96389	0.96389	0.9507	0.9516	0.9542	0.9584
80.00	1.60000	0.97240	0.96339	0.96803	0.96803	0.9561	0.9569	0.9592	0.9630
81.00	1.62000	0.97565	0.96754	0.97167	0.97167	0.9609	0.9617	0.9638	0.9672
82.00	1.64000	0.97855	0.97126	0.97501	0.97501	0.9653	0.9660	0.9679	0.9710
83.00	1.66000	0.98114	0.97460	0.97793	0.97793	0.9693	0.9699	0.9716	0.9743
84.00	1.68000	0.98345	0.97758	0.98059	0.98059	0.9728	0.9733	0.9749	0.9773
85.00	1.70000	0.98549	0.98026	0.98296	0.98296	0.9760	0.9765	0.9778	0.9800
86.00	1.72000	0.98731	0.98264	0.98503	0.98503	0.9788	0.9792	0.9805	0.9824
87.00	1.74000	0.98891	0.98476	0.98689	0.98689	0.9814	0.9817	0.9828	0.9846
88.00	1.76000	0.99032	0.98664	0.98854	0.98854	0.9836	0.9840	0.9849	0.9865
89.00	1.78000	0.99158	0.98830	0.99002	0.99002	0.9856	0.9859	0.9868	0.9882
90.00	1.80000	0.99267	0.98979	0.99125	0.99125	0.9874	0.9877	0.9884	0.9897
91.00	1.82000	0.99364	0.99109	0.99239	0.99239	0.9890	0.9892	0.9899	0.9910
92.00	1.84000	0.99448	0.99224	0.99341	0.99341	0.9904	0.9906	0.9912	0.9922
93.00	1.86000	0.99524	0.99325	0.99429	0.99429	0.9916	0.9918	0.9923	0.9932
94.00	1.88000	0.99589	0.99414	0.99505	0.99505	0.9927	0.9929	0.9933	0.9941
95.00	1.90000	0.99644	0.99491	0.99569	0.99569	0.9937	0.9938	0.9942	0.9949
96.00	1.92000	0.99694	0.99560	0.99628	0.99628	0.9945	0.9946	0.9950	0.9955
97.00	1.94000	0.99737	0.99620	0.99679	0.99679	0.9952	0.9953	0.9957	0.9962
98.00	1.96000	0.99776	0.99672	0.99725	0.99725	0.9959	0.9960	0.9962	0.9967
99.00	1.98000	0.99808	0.99717	0.99768	0.99768	0.9964	0.9965	0.9968	0.9971
100.00	2.00000	0.99835	0.99757	0.99797	0.99797	0.9969	0.9970	0.9972	0.9975

CHAPTER 8

THE FICKIAN PARTICLE DIFFUSION MODEL (HIXM) - HYBRID COMPUTER SOLUTION

Digital computer methods were used in the previous chapter to solve the equations of the model IXM of the fixed-bed ion exchange process. A hybrid computer solution HIXM of these same equations is presented in this chapter, which shows some advantages in speed and stability.

This solution is an extension of the analog computer methods of Chapter 6, but of serial rather than parallel form. The repetition of many identical cells in the pure analog computer solution is quite impossible for the more complex model here. The large complement of equipment required is evaded by patching only one or a few cells on the analog computer and using them recursively to calculate the breakthrough curve a further step down the column from one previously calculated and stored in the digital computer.

The hybrid computation in this and the next chapter was performed on an EAI-590 hybrid computer (Appendix 8A).

8-1 The Hybrid Computer Solution, HIXM

The equations and the initial and boundary conditions are those listed in Table 7-1.

The general method of solution is shown in Figure 8-1. If the breakthrough curve for N transfer units, $x_N(T)$, is stored in the digital computer, it can be used with the profiles $x_{N+\Delta N}$ and perhaps $x_{N+2\Delta N}$ to approximate $\frac{\partial x}{\partial N}$ and hence $\frac{\partial \bar{y}}{\partial T}$.

Similarly, finite difference approximations for $\frac{\partial^2 y}{\partial R^2}$ and $\frac{\partial y}{\partial R}$ reduce the parabolic partial differential equation (Eqn 7-3) to a set of ordinary differential equations of form:-

$$\frac{dy_i}{dT} = ay_{i+1} + by_i + cy_{i-1}$$

where a,b,c are constants and y_i is the resin concentration at the ith pivotal point.

These equations for $\bar{y}$ and all the y_i are functions of the charact-

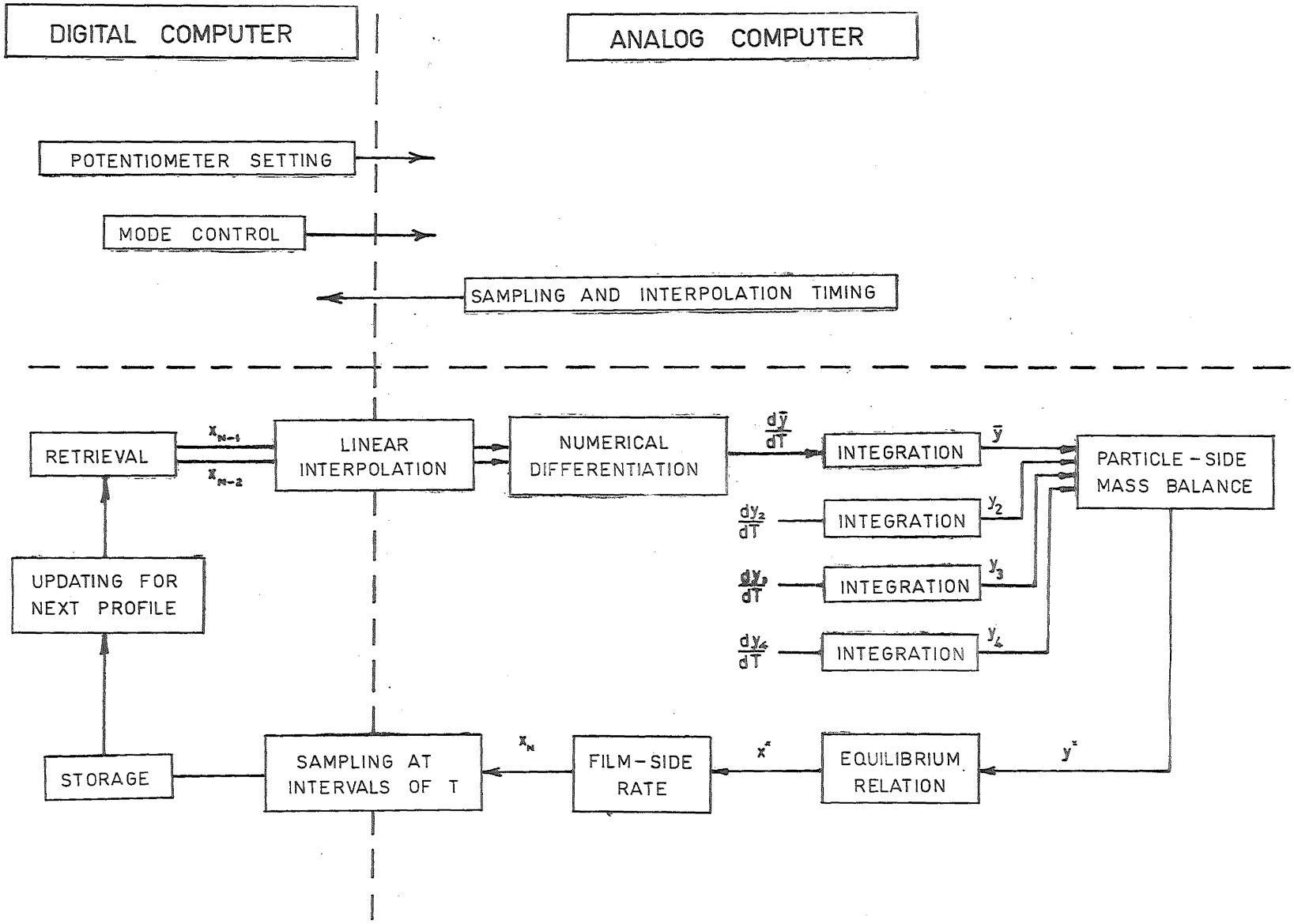


FIGURE 8-1. THE GENERAL METHOD OF THE HYBRID COMPUTER SOLUTION.

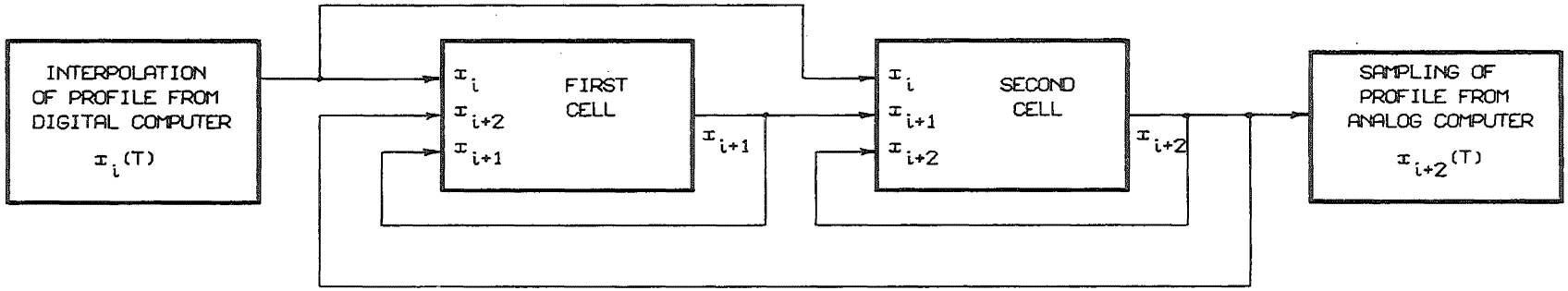


FIGURE 8-2. THE RELATION OF THE TWO CELLS PATCHED IN THE ANALOG SECTION OF THE HYBRID COMPUTER SOLUTION.

eristic time and integrated by the analog computer. The interfacial resin concentration, y*, is obtained from the particle mass belance (Eqn 7-11), and the solution interfacial concentration, x*, is in equilibrium (Eqn 7-5). The new breakthrough curve $x_{N+\Delta N}$ is continuously computed from the solution-side rate equation (Eqn 7-2):-

$$x_{N+\Delta N}(T) = x^*_{N+\Delta N}(T) + \frac{1}{\rho} \left(\frac{d\bar{y}}{dT}\right)_{N+\Delta N}$$

The analog computer takes the breakthrough curve $x_N(T)$ and, from it, calculates a series of profiles, $y_i(T)$, $\bar{y}(T)$, $y^*(T)$, $x^*(T)$ and finally the new breakthrough curve, $x_{N+\Delta N}(T)$, one further step down the column. This curve is stored in the digital computer for the next sweep, yet another step further down the column.

The computation begins with the first sweep driven by the concentration history at the top of the column (N = 0), corresponding to the initial conditions.

Sufficient equipment was available on the analog computer to implement two cells so that each sweep moved a further $2\Delta N$ down the column. Figure 8-2 shows that only a single profile need be transfered between the computers while still maintaining second order accuracy.

Since the digital computer stores the continuous breakthrough curves as discrete values, a system was needed to enable the analog output to be sampled at fixed and accurate intervals of time (or T). Conversely, these discrete values must be returned to the analog computer as a continuous interpolated function. These interface problems are discussed in Section 8-3 and Appendix 8C, and were solved using timing components on the analog computer and the logic of the digital computer.

8-2 The Analog Formulation of the Equations

The basic equations of Table 7-1 must be modified to a form suitable for hybrid computation (Appendix 8B).

8-2-1 The Solution Mass Balance

Eqn 8-1 can be used with either of two differential approximations (Hausner, 1971) as appropriate to either the first or the second cell (Figure 8-2):-

$$\text{First cell} \quad \left.\frac{dx}{d\bar{N}}\right|_{N+\Delta N} = \frac{x_{N+2\Delta N} - x_N}{2\Delta N} + O(\Delta N)^3 \tag{8-1a}$$

$$\text{Second cell} \quad \left.\frac{dx}{d\bar{N}}\right|_{N+2\Delta N} = \frac{3x_{N+2\Delta N} - 4x_{N+\Delta N} + x_N}{2\Delta N} + O(\Delta N)^3 \tag{8-1b}$$

When substituted into the solution mass balance, the equations which result:-

$$\left.\frac{d\bar{y}}{d\bar{T}}\right|_{N+\Delta N} = -\frac{1}{2\Delta N}(x_{N+2\Delta N} - x_N) \tag{8-2a}$$

$$\left.\frac{d\bar{y}}{d\bar{T}}\right|_{N+2\Delta N} = -\frac{1}{2\Delta N}(3x_{N+2\Delta N} - 4x_{N+\Delta N} + x_N) \tag{8-2b}$$

can be continuously integrated to give the $\bar{y}$ functions.

8-2-2 The Particle Rate Equation

It was shown in Section 7-5 that the digital computer solution of Eqn 7-3 (or the finite difference form, Eqns 7-6, 7-7) require no more than four radial elements. An analog computer typically requires fewer elements, presumably because the integration in the T direction is continuous. Consequently four radial elements have again been used for this hybrid simulation.

The equations become:-

$$\begin{aligned}
\frac{dy_2}{d\bar{T}} &= \frac{16\sigma}{15}(2y_3 - 2y_2) \\
\frac{dy_3}{d\bar{T}} &= \frac{16\sigma}{15}\left(\frac{3}{2}y_4 - 2y_3 + \frac{1}{2}y_2\right) \\
\frac{dy_4}{d\bar{T}} &= \frac{16\sigma}{15}\left(\frac{4}{3}y_5 - 2y_4 + \frac{2}{3}y_3\right)
\end{aligned} \tag{8-3}$$

These equations can be integrated to give y_2, y_3, y_4 as functions of

the characteristic time in each cell. The profile y_1 is not required either in Eqns 8-3 or in the mass balance.

8-2-3 The Particle-side Mass Balance

The integrated form of this equation (Eqn 7-4) is used with 4 radial elements (Eqn 7-11) to give

$$y^* = 4\bar{y} - \frac{y_2}{4} - \frac{y_3}{2} - \frac{9}{4} y_4 \qquad (8\text{-}4)$$

8-2-4 The Equilibrium Relation

The equilibrium relation (Eqn 7-5) was modified to:-

$$x^* = \frac{\frac{G}{K} y^*}{G(1-y^*) + \frac{G}{K}y^*} \qquad (8\text{-}5)$$

so that the analog computer circuit used would apply both for favourable and unfavourable equilibrium without physical repatching. The value of the dummy variable G is given by:-

K	< 1.0	1.0	> 1.0
G	K	1.0	1.0

8-2-5 The Film-side Rate Equation

Eqn (8-2) is used in the form:-

$$x = x^* + \frac{1}{\rho} \frac{d\bar{y}}{dT} \qquad (8\text{-}6)$$

for both cells.

8-3 SAMPLING AND INTERPOLATION

The function $x_N(T)$ is stored in the digital computer as a series of point values. For use in the analog computer it is restored to a continuous function with a simple analog circuit using linear interpolation between sample points. Strictly, this does not provide a smooth function (there will be corners in the function at the sample points) but the integrators in the simulation smooth the solution, particularly as the points are close.

The continuous breakthrough curve $x_{N+2\Delta N}(T)$ produced by the analog computer is sampled and replaces the profile in the digital computer. The function is captured on a track/store unit, sampling for 100μsec at intervals of 50 msec. Further details are given in Appendix 8C.

8-4 THE DIGITAL COMPUTER PROGRAM

The main features of the digital computer program are shown in the block diagram, Figure 8-3, while the subprogram SWEEP which controls the analog computer during a single sweep, updating the stored profile from x_N to $x_{N+2\Delta N}$, is shown in Figure 8-4.

These main programs were written in Fortran (Appendix 8D). A number of other programs were written in EAI-640 assembler to control the analog computer (to set potentiometers, D/A converters, and control lines, to control the analog mode and to read values on components) and are not included as they are specific to that machine and the local configuration.

The computed breakthrough curves were displayed on a Tektronics 611 storage oscilloscope. A permanent record could be obtained from an X-Y plotter, or more quickly by punching breakthrough curve points on paper-tape, to be later processed by the IBM 360/44 giving the graphs included with this chapter.

8-4-1 Step-Size Selection

In this solution there were two step-sizes to establish:-

(i) The step-size down the profile, DELT, the sample spacing to express the continuous function from the analog computer as a vector of point values.

(ii)The step-size between profiles, DELN, which should be small to maintain the accuracy of the finite-difference approximations (Eqns 8-1) but large to speed computation.

The step-size in N also affects accuracy, in that it determines the number of sweeps necessary to attain a given number of transfer units. The more times profiles are passed between the two computers, the greater the random errors become. To minimise the number of sweeps (and also the length of a sweep) both step-sizes are set small at the top of the column where the breakthrough curve gradients are large, and are doubled several times (up to certain maximum values DELTMX and DELNMX) as the

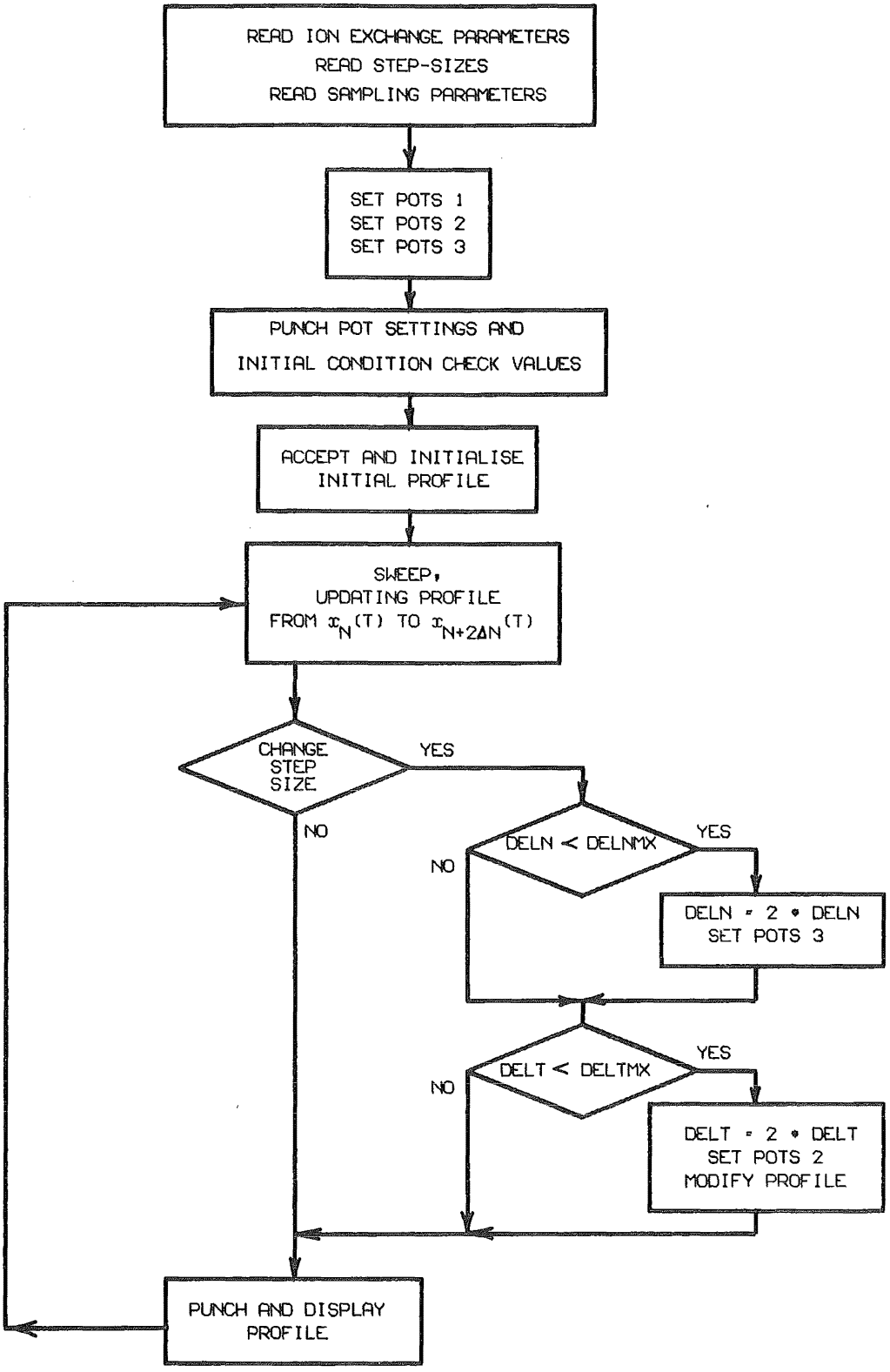


FIGURE 8-3. FLOW SHEET FOR DIGITAL COMPUTER SECTION OF HIXM.

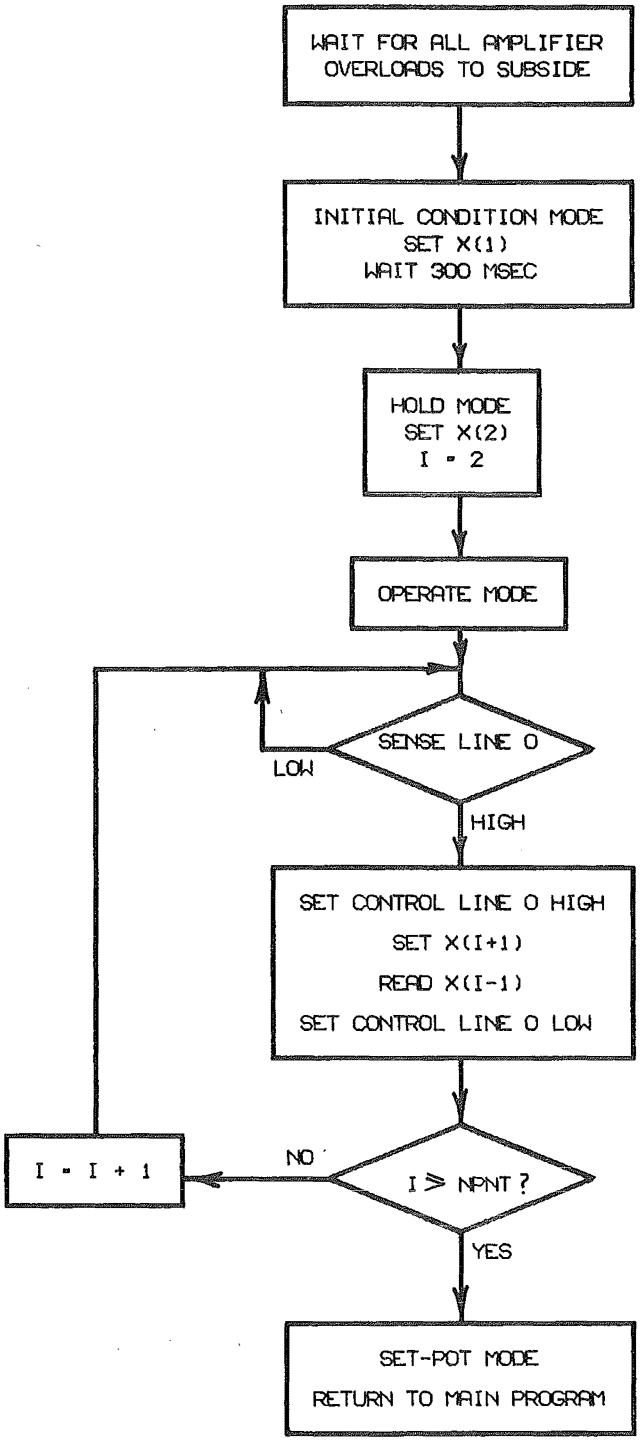


FIGURE 8-4. FLOW SHEET FOR THE SWEEP SUBPROGRAM.

program works down the column.

The decision to change the step-size was taken at the end of a sweep and was based on the value of the computed breakthrough curve at a characteristic time 90% of the width of the present sweep. If that value were greater than 0.99 (or if the maximum step-sizes had been reached) then the step-size was not changed.

The manipulation of DELT is related to the time-scaling of the analog computer and is discussed in Appendix 8C.

There are feedback loops in the analog circuit (Fig. 8B-1) which contain no integrator. If the gain in these loops is greater than a critical value ($\sec^{n}(\frac{\pi}{n})$, where n is the number of amplifiers in the loop, Wilkins, 1970) the analog computer will become unstable. These loops (two for each cell) are shown in Figure 8-5, and the smallest step-size for analog computer stability is 0.59 (in accord with experience). However, larger step-sizes than this were used and no stability problem occurred.

Step-sizes were generally established for each set of model parameters (i.e. K and ξ) by reducing step-size until successive runs, viewed on the storage oscilloscope, were indistinguishable. As experience developed, the following values were established:-

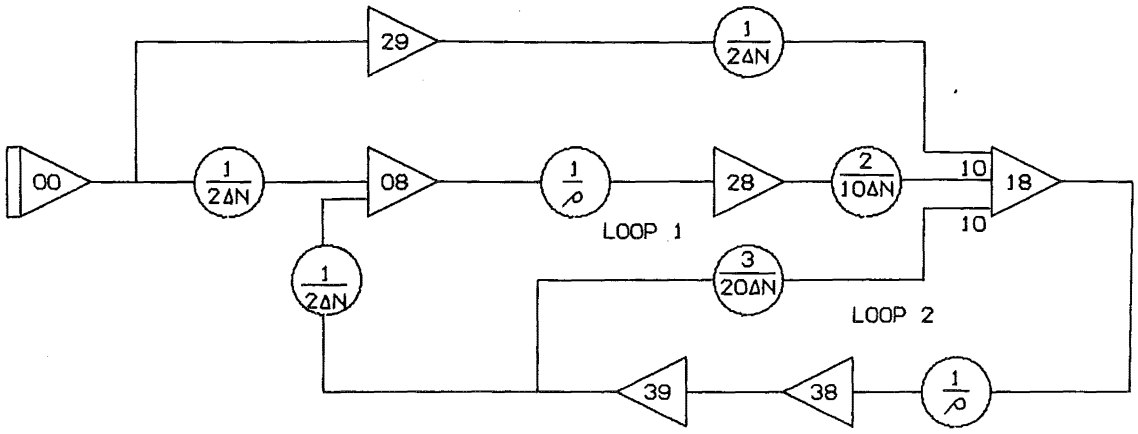
K	DELN	DELNMX	DELT	DELTMX	NPNT
$\leq$ 1	1.0	4.0	0.25	2.0	100
1.2	1.0	2.0	0.25	2.0	100
$\geq$ 2	1.0	2.0	0.125	2.0	200

Smaller step-sizes were required if the equilibrium was sufficiently favourable to establish steep breakthrough curves.

8-5 VERIFICATION OF HIXM

In many respects, computed results should be treated in the same way as experimental data, and this is especially so for results generated by a hybrid computer, where the accuracy of components (at best 0.01%) can introduce both random and systematic errors.

The computed results from HIXM can be verified against analytical



	LOOP 1	LOOP 2
LOOP GAINS	$\frac{1}{\rho}\cdot\frac{2}{10\Delta N}\cdot\frac{1}{\rho}\cdot\frac{1}{2\Delta N}\cdot\frac{10}{1}$	$\frac{3}{20\Delta N}\cdot\frac{10}{\rho}$
	$\frac{1}{\rho^2\Delta N^2}$	$\frac{3}{2\Delta N\rho}$
NUMBER OF AMPLIFIERS	5	3
GAIN LIMIT	2.9	8.0
LIMIT ON N	$\Delta N > \frac{0.59}{\rho}$	$\Delta N > \frac{0.19}{\rho}$

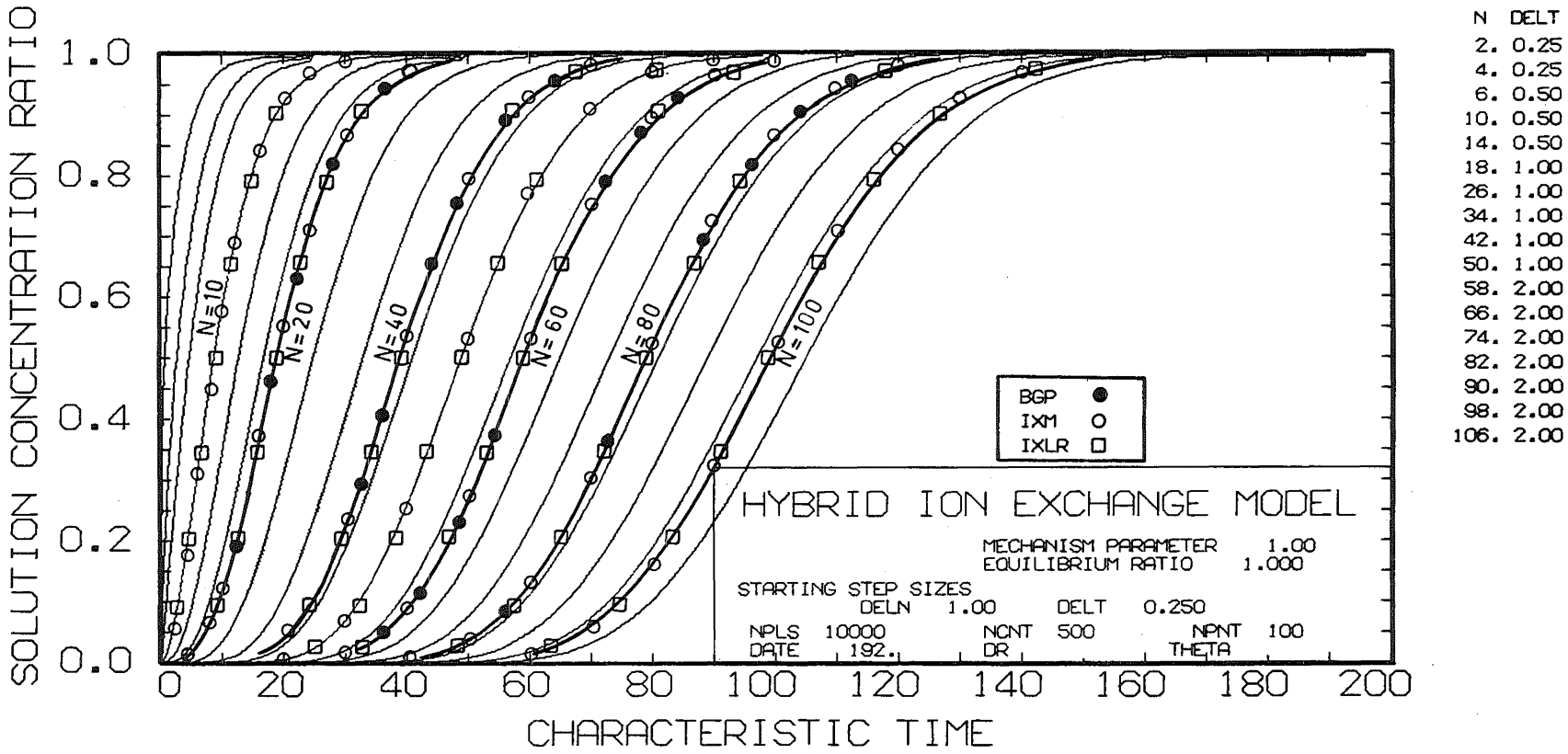
FIGURE 8-5. LIMITS ON STEP-SIZE IMPOSED BY ALGEBRAIC FEEDBACK LOOPS.

results for linear equilibrium in the same way as were the digital computer programs. In addition, HIXM can be tested against those programs already verified, particularly IXM which solves exactly the same equations. Any faults in the digital program, in the interface between the computers, in the patching and programming of the analog computer or systematic errors in the computing components should then be revealed.

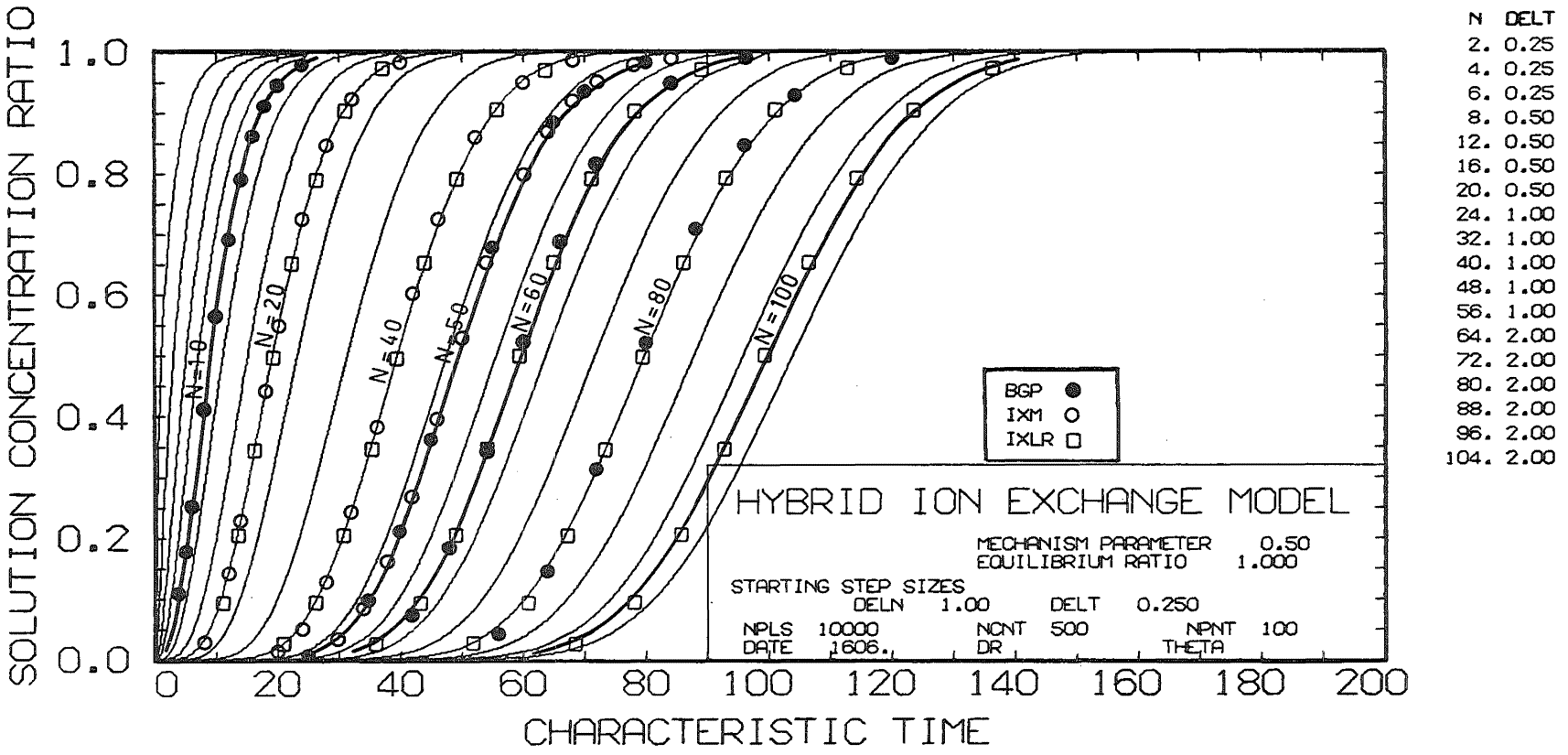
Graph 8-1 compares the results for the "standard" conditions ($K = 1.0, \xi = 1.0$) with those from the BGP and IXM programs. This graph (as with all those giving hybrid computer results) has been directly prepared from paper tape punched as the solution was being computed. As a result, breakthrough curves are shown at transfer units that depend on when the step-size was doubled. Further, by the doubling process, the curves are spaced by 2,4 or 8 units. Since the breakthrough curves from IXM and IXLR were collected at 10(10)100 transfer units, some interpolation was necessary to give correspondence. For instance, in Graph 8-1, the breakthrough curves for N = 10 and 50 are easily compared but the breakthrough curves for N = 20,40,60,80,100 have had to be interpolated. As can be seen this is easily and accurately done by hand.

Equally good agreement was obtained for other values of the mechanism parameter. Graphs 8-2 and 8-3 make the same comparisons for $\xi = 0.5$ and 10.0, while Graph 8-4 is of particular interest with $\xi = 0.1$, since this is the region for which IXM had stability difficulties requiring small step-sizes and extensive computing time. As a result, the points shown are from BGP and IXLR only. The quality of agreement here suggests that the results of HIXM (and consequently IXM) are equivalent to those of IXLR supporting the contention that the linear particle rate expression (Eqn 2-7) is adequate for ion exchange column studies. Further results are examined in Section 8-6.

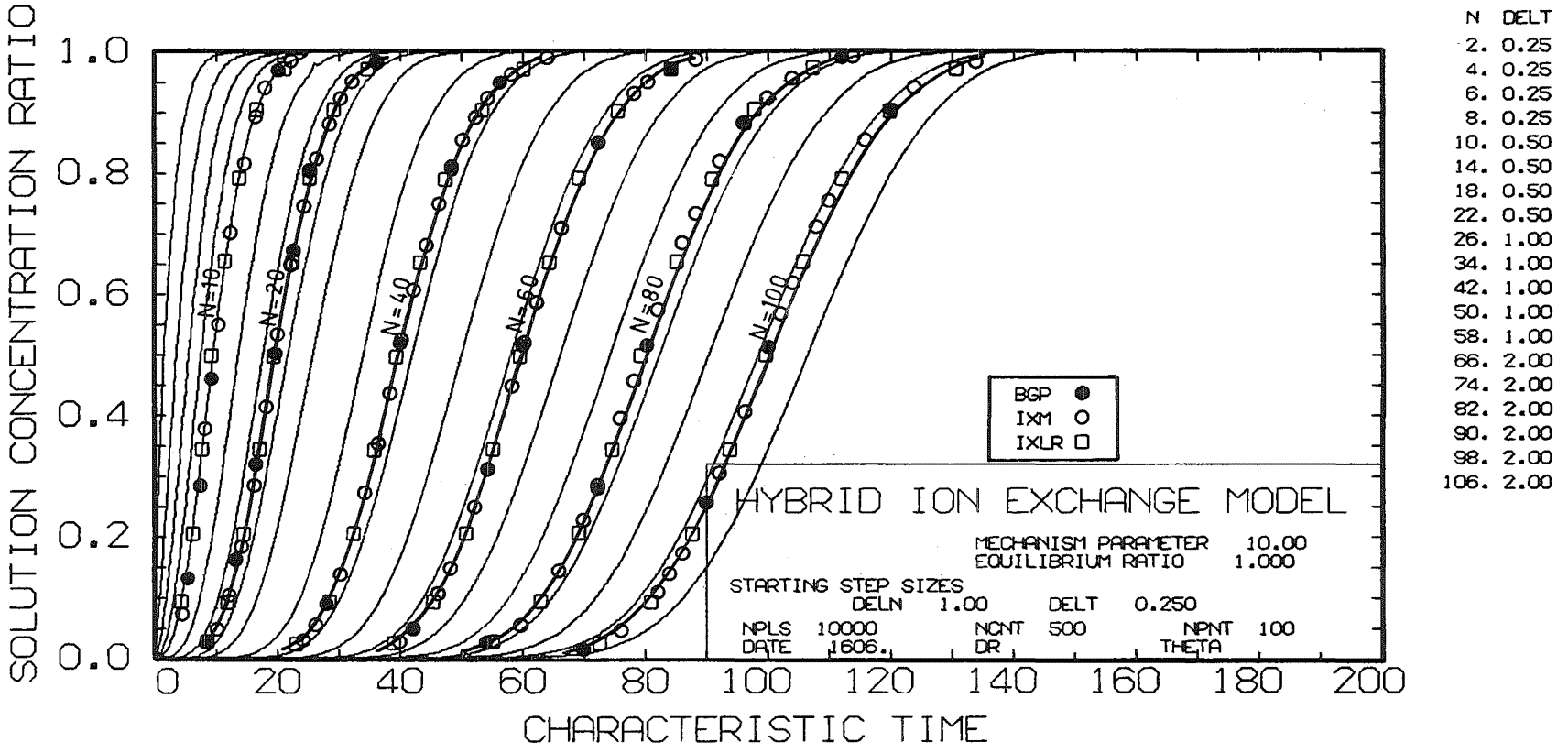
For non-linear equilibrium, the results of HIXM were compared with those of IXM; Graph 8-5 for favourable ($K = 1.2, \xi = 1.0$) and Graph 8-6 for unfavourable equilibrium ($K = 0.5, \xi = 1.0$). This last graph shows HIXM with arbitrary boundary conditions, in this case exhaustion followed immediately by regeneration:-



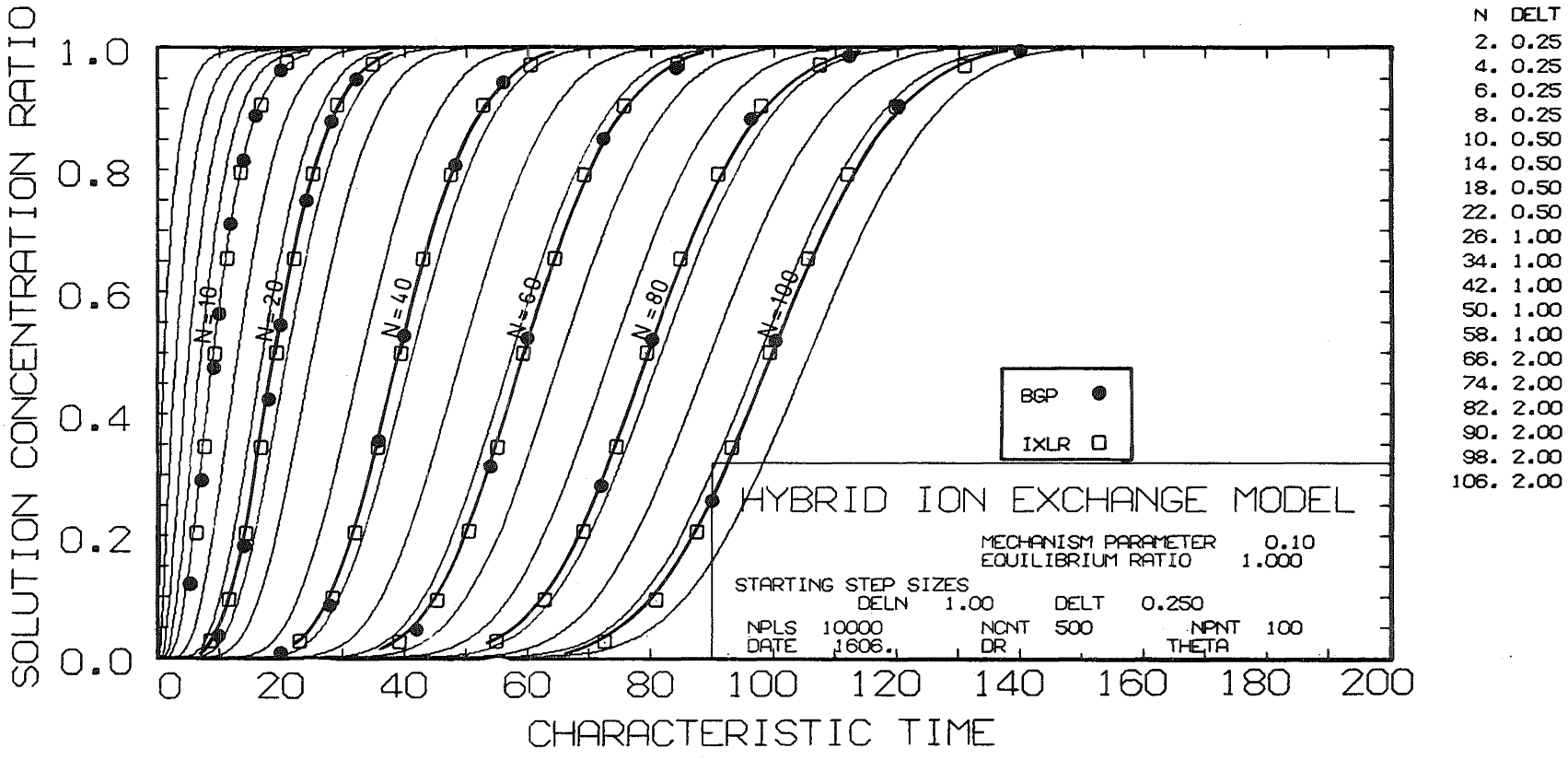
GRAPH 8-1. VERIFICATION OF HIXM AGAINST BGP AND IXM FOR LINEAR EQUILIBRIUM. IXLR RESULTS ARE INCLUDED FOR COMPARISON.



GRAPH 8-2. VERIFICATION OF HIXM AGAINST BGP AND IXM FOR LINEAR EQUILIBRIUM. IXLR RESULTS ARE INCLUDED FOR COMPARISON.



GRAPH 8-3. VERIFICATION OF HIXM AGAINST BGP AND IXM FOR LINEAR EQUILIBRIUM. IXLR RESULTS ARE INCLUDED FOR COMPARISON.



GRAPH 8-4. VERIFICATION OF HIXM AGAINST BGP FOR LINEAR EQUILIBRIUM. RESULTS FROM IXLR ARE INCLUDED FOR COMPARISON.

$$x_{N=0} = 1.0 \qquad 0 \leqslant T \leqslant 100.0$$

$$x_{N=0} = 0.0 \qquad T > 100.0$$

The agreement between HIXM on the one hand and analytical and computed results on the other is sufficiently good (certainly better than ± 0.01 in x) to justify accepting the results of the hybrid computer as solutions to the equations of the model. Some estimate of their variability should be made.

Table 8-1 contains results for replications of "standard" conditions, as defined in Graph 8-1. These conditions were used to generate test runs of the hybrid computer before any final results were collected to check the computing system. The accuracy of the hybrid computer and of the method of solution can be judged from this table.

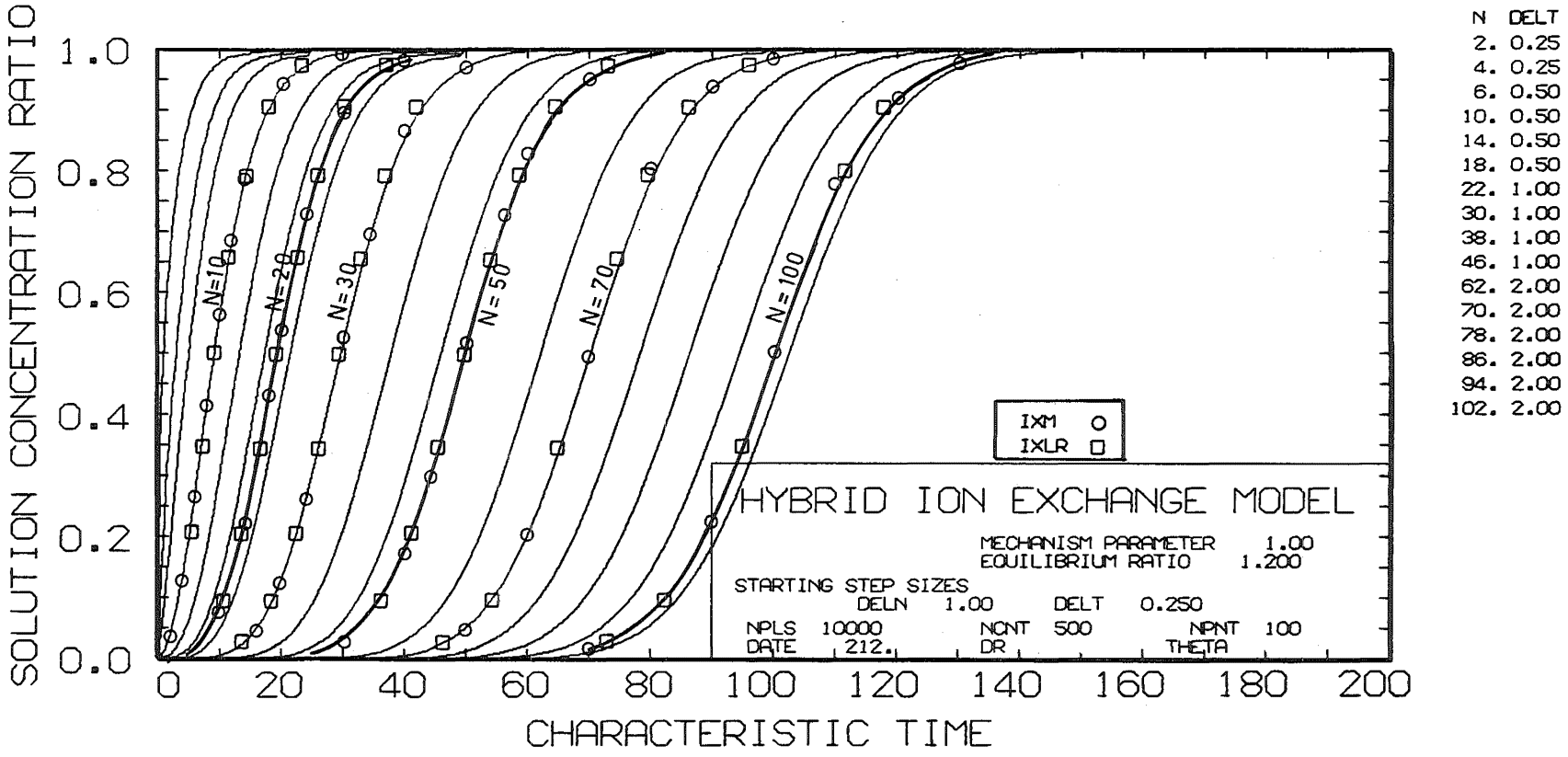
The standard deviation of the results is less at the ends of the breakthrough curve (naturally enough because of the limiting processes involved) and rather more at 80 transfer units after an increased number of sweeps. Consequently, the results produced by HIXL contain a random error about ± 0.007 in general, rather less for small or large x, and rather greater for a large number of transfer units.

The breakthrough curves predicted by the hybrid computer method and by the other methods are in agreement to these limits, and so HIXL can be considered verified.

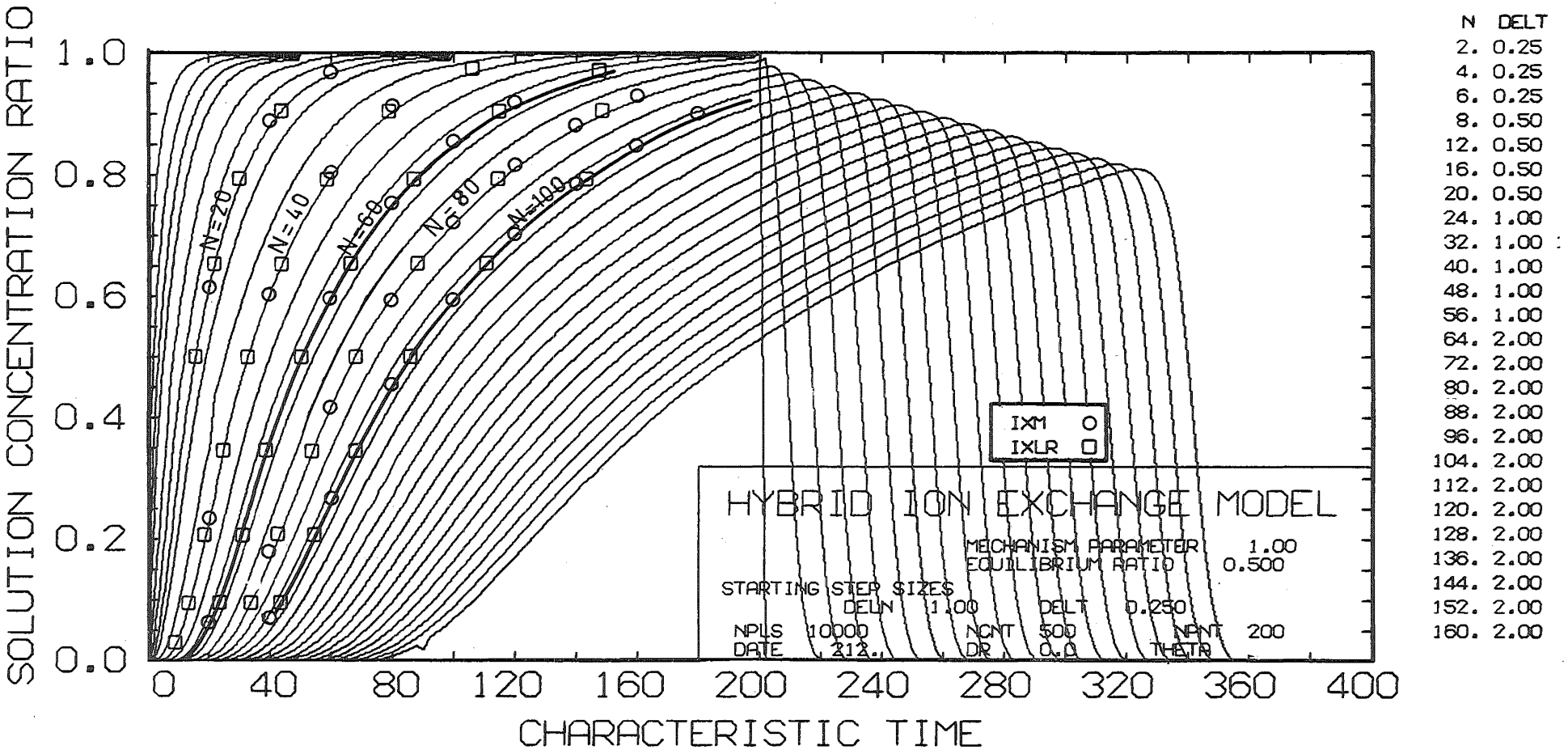
The attainable accuracy of the hybrid program is inferior to that attainable from the digital computer solutions; for instance, IXLR approaches the J function within ± 0.0002 with complete reproducibility, errors stemming from computational approximation. The hybrid computer has in addition the random errors of analog performance and measurement very similar in type to those arising in an experimental study of fixed-bed ion exchange breakthrough behaviour, although still less in magnitude.

8-6 HIXM RESULTS

In Chapter 7, the results of the program IXLR were compared with those of IXM, for values of the mechanism parameter greater than 0.5, the lower limit of IXM for reasonable computing time. The results of



GRAPH 8-5. VERIFICATION OF HIXM AGAINST IXM FOR FAVOURABLE EQUILIBRIUM. RESULTS FROM IXLR ARE INCLUDED FOR COMPARISON.



GRAPH 8-6. VERIFICATION OF HIXM AGAINST IXM FOR UNFAVOURABLE EQUILIBRIUM. RESULTS FROM IXLR ARE INCLUDED FOR COMPARISON.

Solution concentration ratios

N = 20

Run	292/1.	222/1.	222/8.	272/7.	262/1.	262/2.	262/3.	262/5.	Standard Deviation
T									
5	.016	.016	.015	.017	.016	.016	.017	.017	0.0007
10	.127	.126	.123	.130	.127	.127	.128	.128	0.0020
20	.562	.562	.561	.569	.564	.563	.563	.564	0.0024
30	.872	.873	.872	.876	.873	.872	.873	.874	0.0014
40	.975	.978	.977	.978	.978	.976	.977	.978	0.0011

N = 40

Run	272/6.	272/7.	262/1.	262/3.	262/5.	
T						
20	.045	.045	.045	.045	.045	0.0
30	.246	.248	.247	.244	.242	0.0016
40	.556	.559	.557	.553	.554	0.0024
50	.810	.812	.810	.807	.808	0.0019
60	.944	.944	.943	.942	.943	0.0010

N = 80

Run	272/6	272/7	262/1	262/3	262/5	
T						
50	.047	.047	.048	.049	.047	0.0009
70	.343	.343	.343	.339	.340	0.0019
80	.562	.560	.560	.554	.556	0.0033
90	.756	.755	.755	.748	.752	0.0033
110	.963	.962	.962	.959	.962	0.0015

TABLE 8-1 The reproducibility of the results of the hybrid computer solution, HIXM.

the two programs were very similar and it was argued that the difference between the two models (the particle rate expression, Eqn 2-5 and Eqn 2-7) was insignificant. The main use of the hybrid computer program has been to extend this observation to still smaller values of the mechanism parameter where the particle phase rate mechanism is more important.

Graphs 8-8 and 8-9 compare hybrid computer results for $\xi = 0.5$ with both IXLR and IXM. All three solutions agree within the standard error of HIXM, with the digital computer methods in slightly better agreement.

Further results for linear and favourable equilibrium are shown in Graphs 8-10 to 8-13, down to full particle control where any deviation between the models HIXM and IXLR should become more marked. Some difference is evident, but none more than that attributable to random error in HIXM.

No significant difference has been established between the models (IXM and HIXM) which use the fickian diffusion expression (Eqn 2-5) and the model IXLR which uses the linear particle rate expression (Eqn 2-7).

8-7 EXTENSION OF THE HIXM MODEL

The HIXM model can be easily extended to include four further effects:-

(a) Generalised boundary conditions.

(b) Generalised initial conditions.

(c) Arbitrary equilibrium relation.

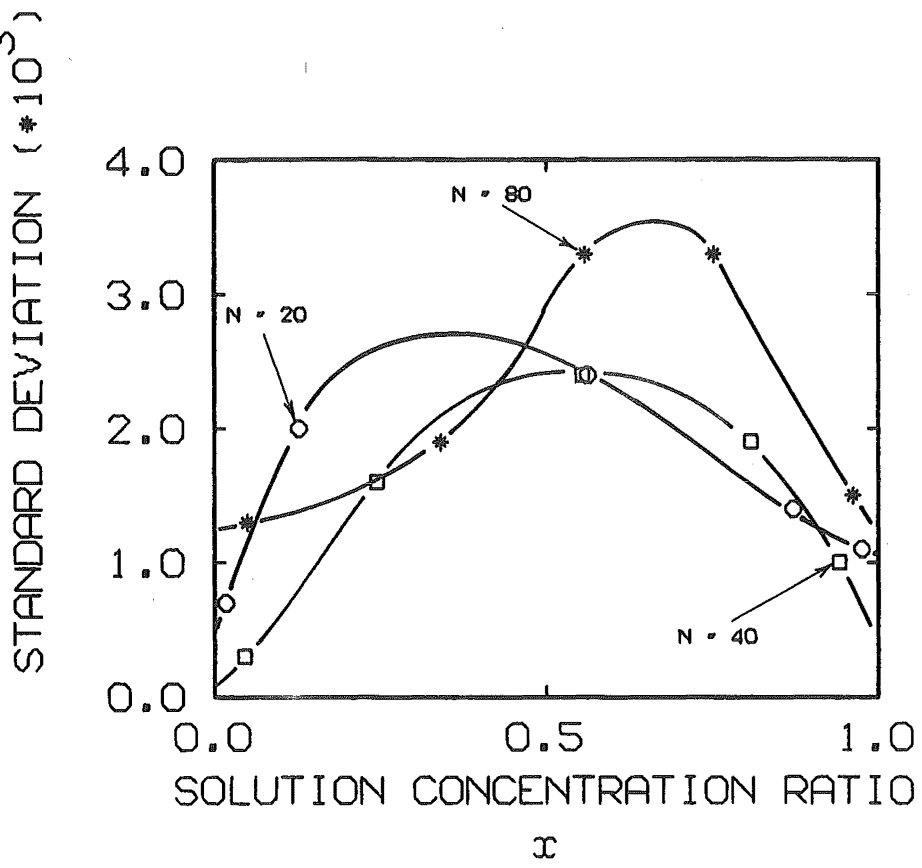
(d) Variable diffusivity.

8-7-1 Boundary Conditions

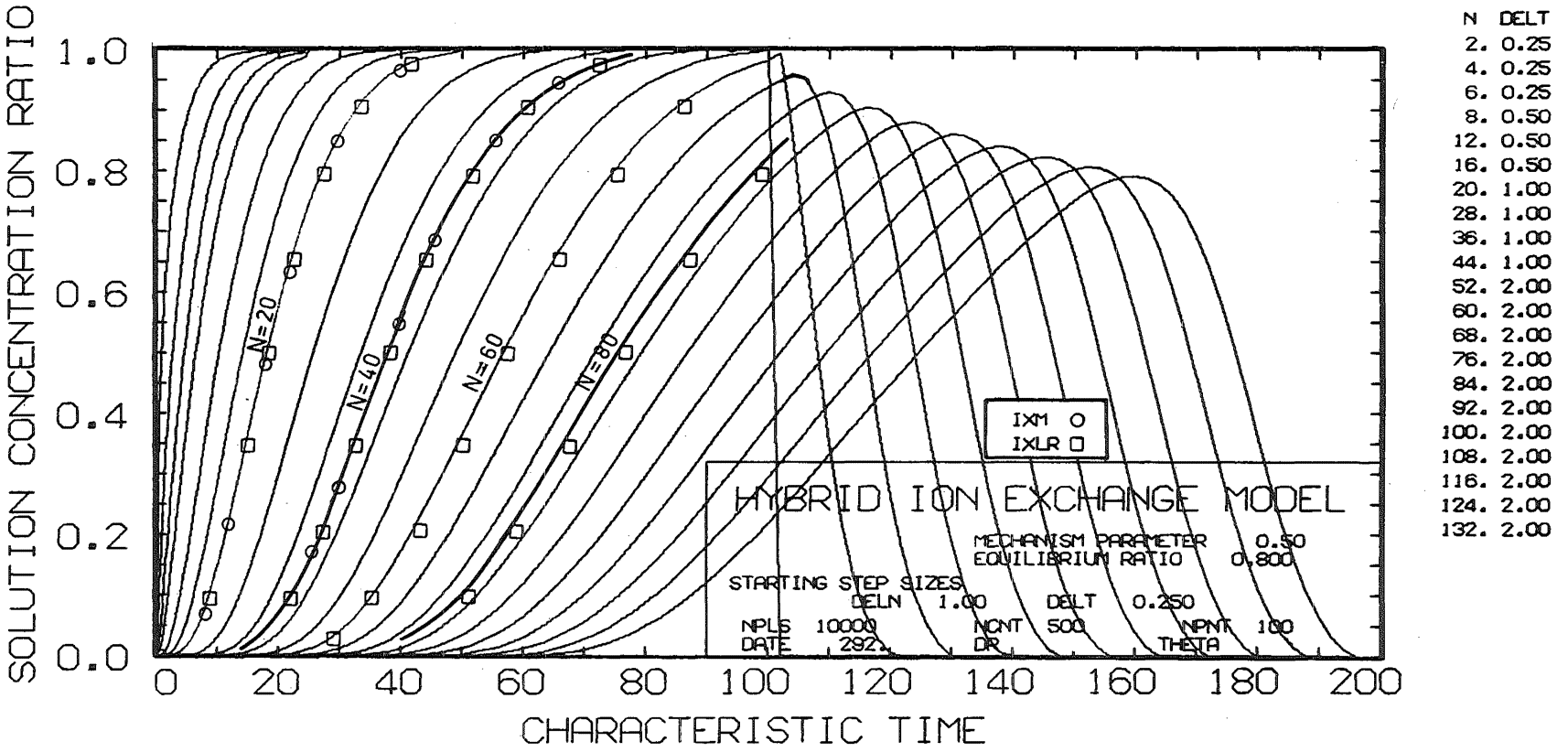
The concentration history has normally been:-

$$x_{N=0} = 1.0 \quad \text{for all T}$$

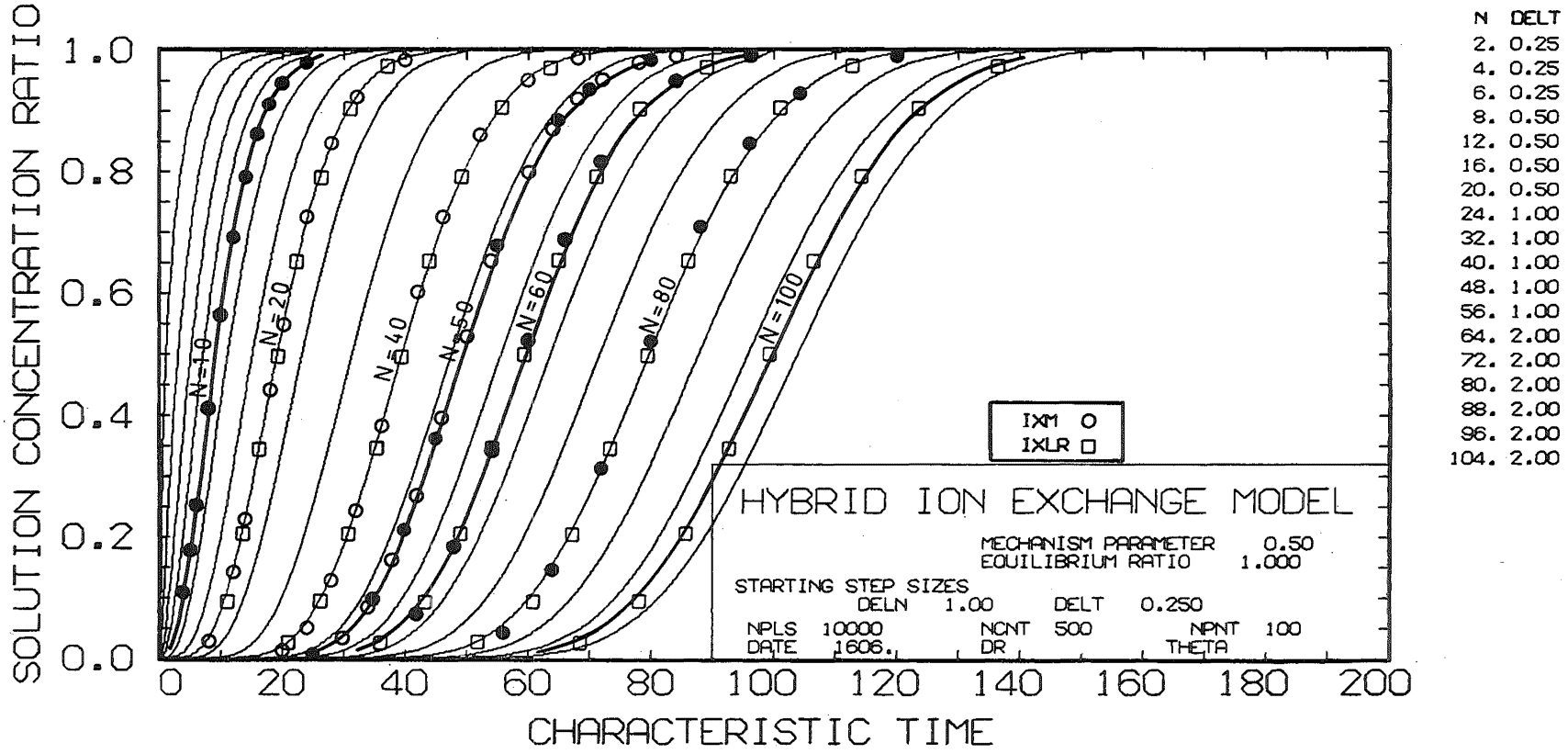
However, any concentration profile can be specified in HIXM. Graphs 8-6 and 8-7 have been included to show the effect of exhaustion followed immediately by regeneration.



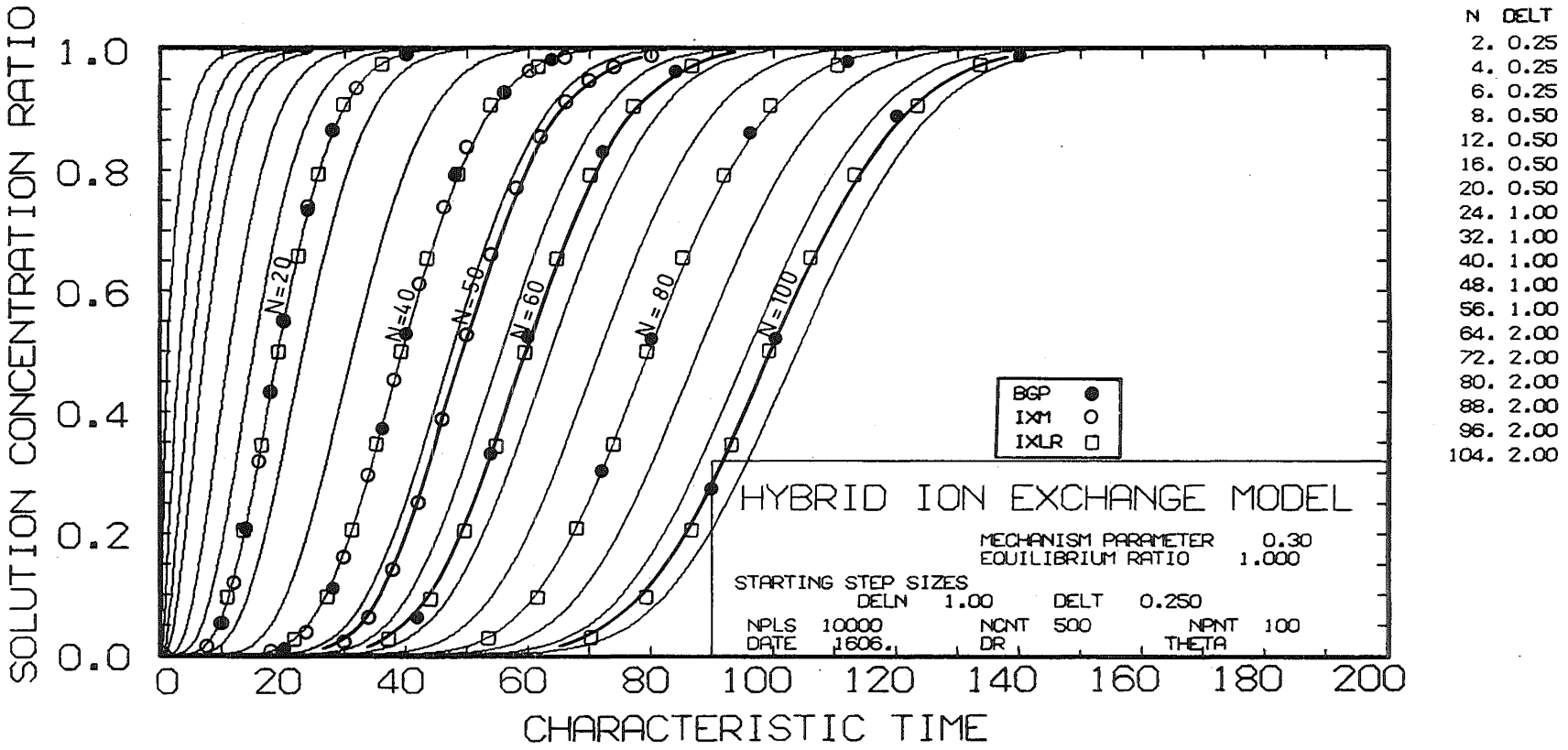
GRAPH 8-7. REPRODUCIBILITY OF HIXM RESULTS.



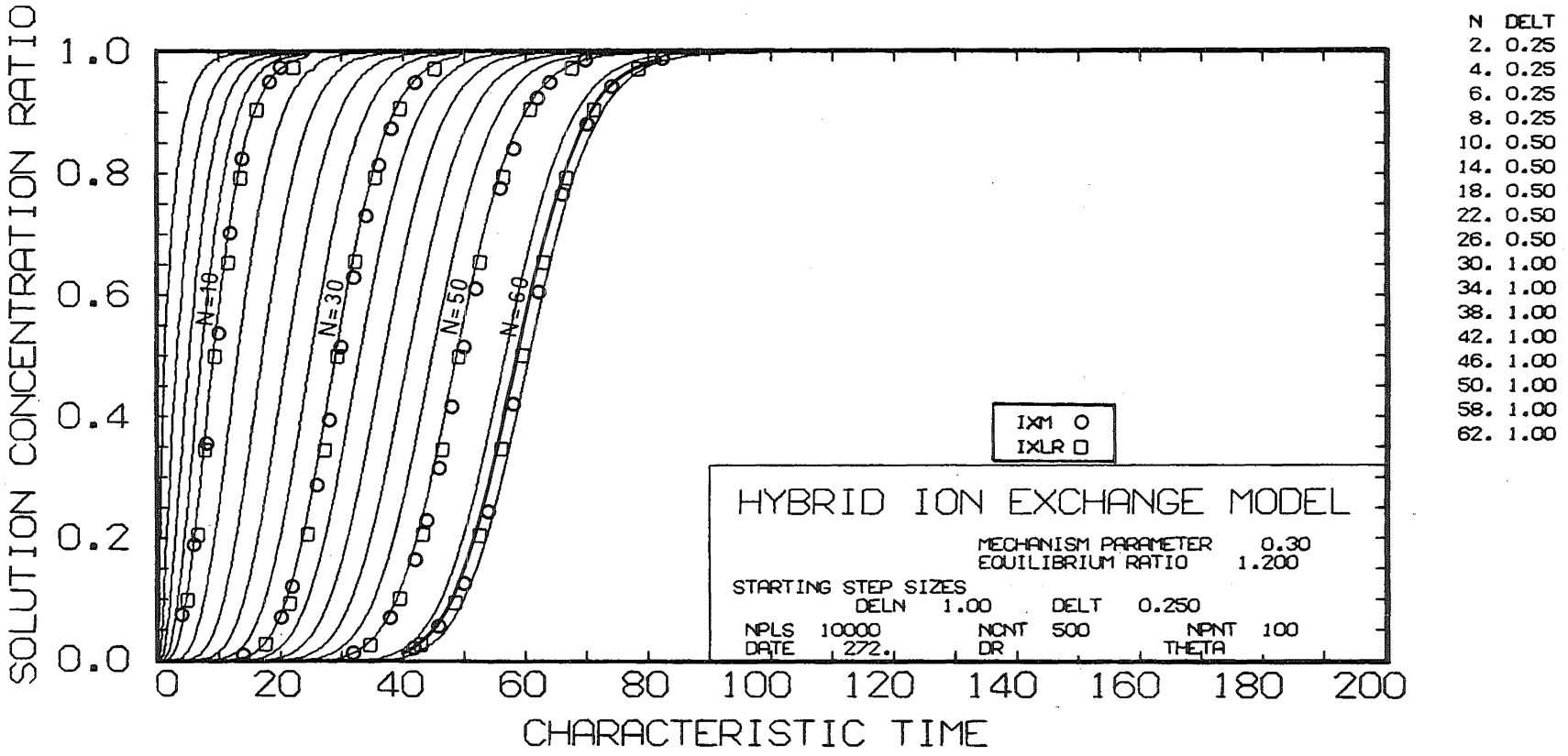
GRAPH 8-8. THE EQUIVALENCE OF COMPUTED RESULTS FROM THE FICKIAN DIFFUSION MODELS (IXM AND HIXM) AND IXLR, THE LINEAR PARTICLE DIFFUSION MODEL.



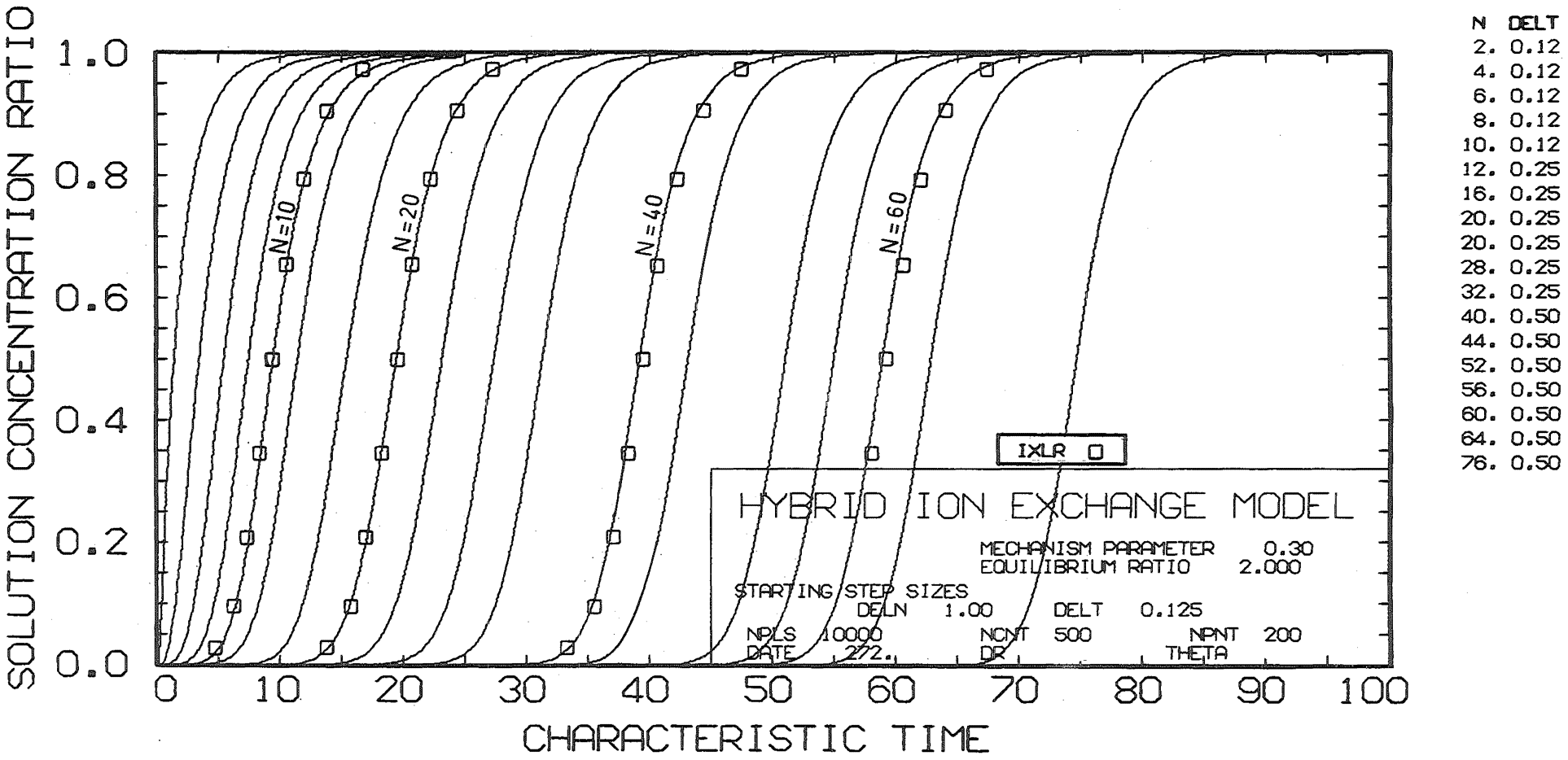
GRAPH 8-9. THE EQUIVALENCE OF COMPUTED RESULTS FROM THE FICKIAN DIFFUSION MODELS (IXM AND HIXM) AND IXLR, THE LINEAR PARTICLE DIFFUSION MODEL.



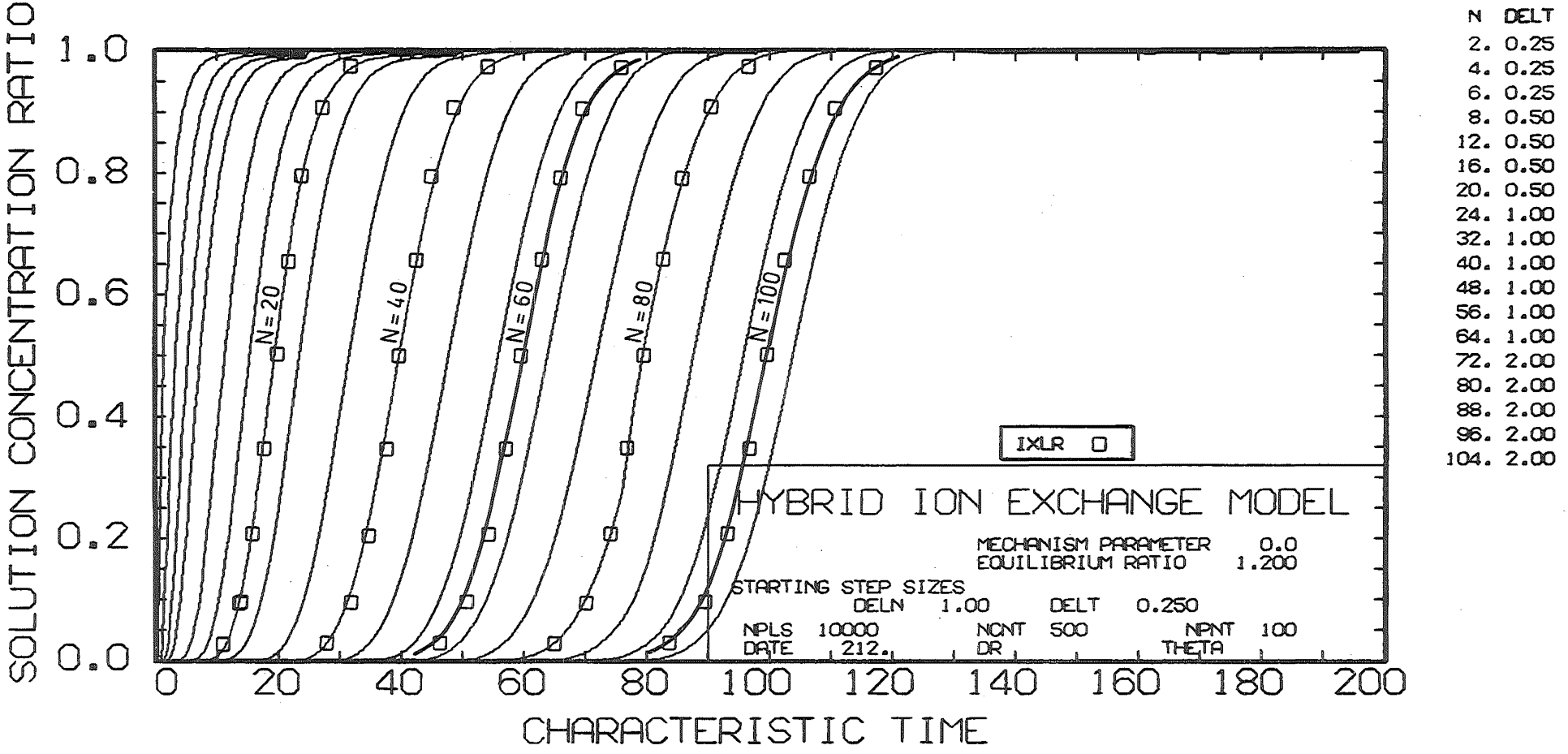
GRAPH 8-10. THE EQUIVALENCE OF COMPUTED RESULTS FROM THE FICKIAN DIFFUSION MODELS (IXM AND HIXM) AND IXLR, THE LINEAR PARTICLE DIFFUSION MODEL.



GRAPH 8-11. THE EQUIVALENCE OF COMPUTED RESULTS FROM THE FICKIAN DIFFUSION MODEL HIXM AND THE LINEAR PARTICLE DIFFUSION MODEL IXLR.



GRAPH 8-12. THE EQUIVALENCE OF COMPUTED RESULTS FROM THE FICKIAN DIFFUSION MODEL HIXM AND THE LINEAR PARTICLE DIFFUSION MODEL IXLR.



GRAPH 8-13. THE EQUIVALENCE OF COMPUTED RESULTS FROM THE FICKIAN DIFFUSION MODEL HIXM AND THE LINEAR PARTICLE DIFFUSION MODEL IXLR.

8-7-2 Initial Conditions

The initial conditions used with HIXM have corresponded to an empty column at T = 0. Any other initial condition could have been applied to the $\bar{y}$ and y_i integrators, either constant for uniform particle presaturation or a function of bed depth.

8-7-3 Arbitrary Equilibrium

A constant separation factor has been assumed in relating x* and y* through Eqn 7-5. If the circuitry to compute this relation (Figure 8B-1, between amplifiers 48 and 28 for the first cell or 58 and 20 for the second cell) is replaced by a variable diode function generator, any arbitrary relation can be used to compute x* from y*.

To test the method, Graph 8-14 compares results from HIXM firstly using a constant separation factor (K = 0.675) and secondly using the function generator set to y*/x* values calculated from Eqn 7-5 for the same value of the separation factor.

Graph 8-15 shows the better fit that could be achieved to Kelly's experimental data (Section 5-6) if his arbitrary equilibrium relation were used for the 0.1 N Na-H system.

8-7-4 Variable Diffusivity

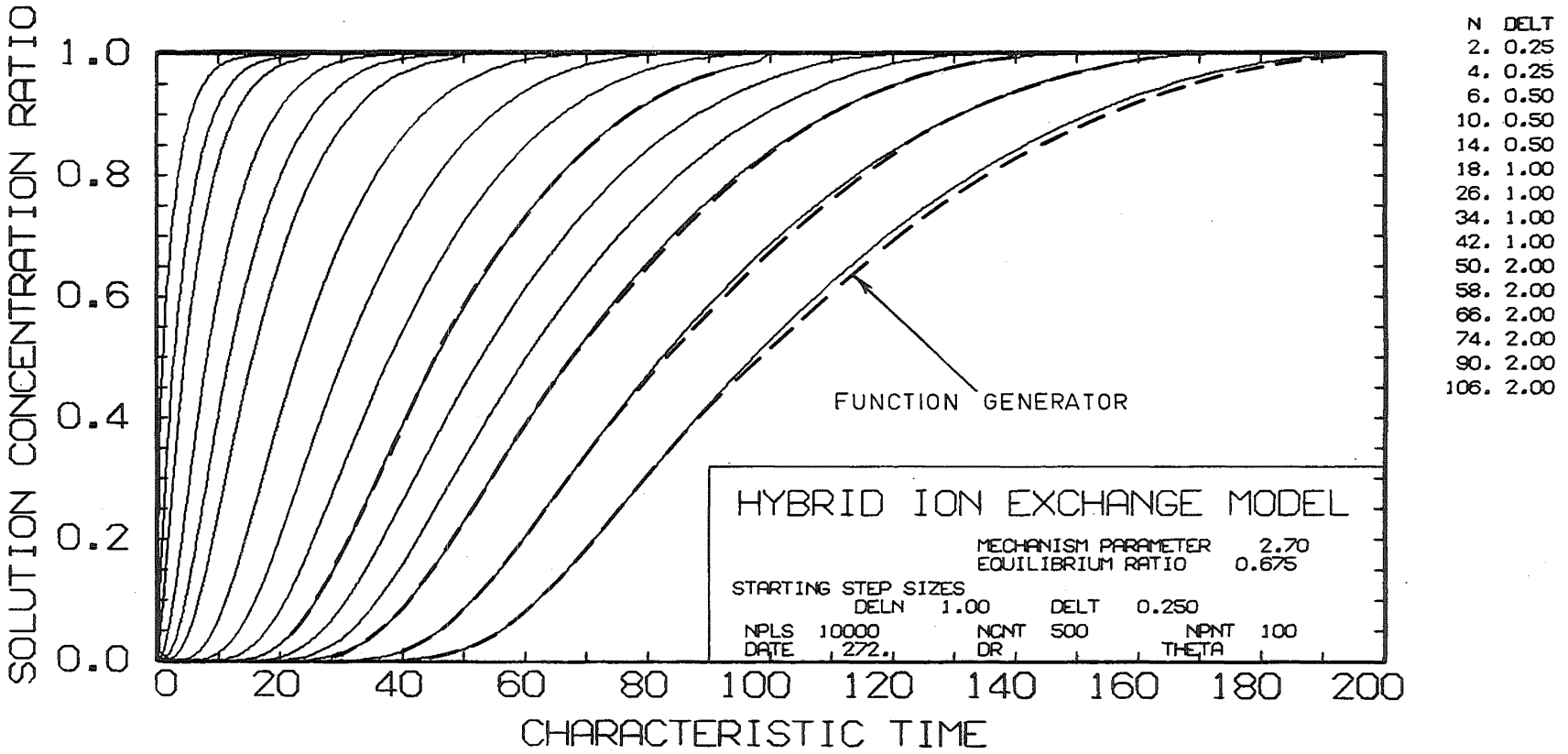
The HIXM model could be converted to variable diffusivity. The number of particle transfer units can be defined in terms of some average diffusivity $\bar{D}_p$ and the definition of the remaining parameters (ξ, σ, ρ, T) need not be changed. A correction factor

$$F = \frac{D_p}{\bar{D}_p}$$

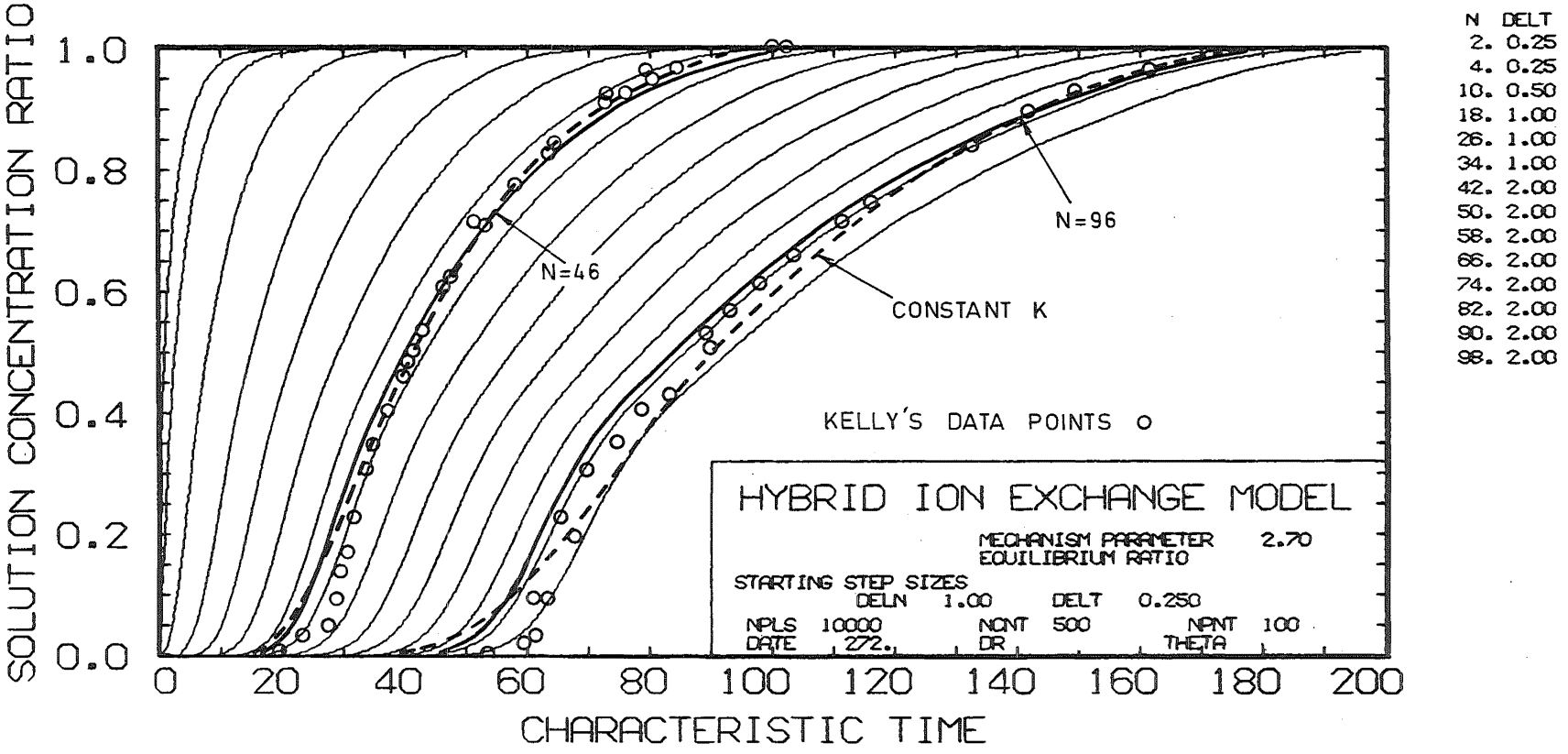
is introduced into Eqn 7-3 which becomes

$$\frac{dy}{dT} = \frac{F\sigma}{15}\left(\frac{\partial^2 y}{\partial R^2} + \frac{2}{R}\frac{\partial y}{\partial R}\right)$$

The potentiometers currently set to $\frac{0.95}{\sigma}$ around amplifiers 42,43,44 (and correspondingly for cell 2) would be set instead to $\frac{0.95}{F\sigma}$, or some similar factor to allow a wider range of F without scaling problems. The value of F would be different for each of the six values involved, and would depend on the associated y_i value. This method could be



GRAPH 8-14. VERIFICATION OF ARBITARY EQUILIBRIUM CALCULATION IN HIXM - COMPARISON AT CONSTANT SEPARATION FACTOR.



GRAPH 8-15. THE IMPROVED HIXM REPRESENTATION OF KELLY'S (1966) EXPERIMENTAL RESULTS (RUNS 74-76) USING AN ARBITARY EQUILIBRIUM RELATION.

implemented by replacing the potentiometers by multiplying digital to analog converters set by the digital computer at each step in a sweep after reading the y_i values and computing the appropriate F value.

No attempt has been made to investigate this effect. One of the conclusions of this thesis is that the diffusion equation, Eqn 7-3, represents an unnecessary refinement over the linearised form, Eqn 2-7, for ion exchange column simulation. The further complexity of a variable diffusivity in Eqn 8-3 would be even less significant.

8-8 THE USE OF THE HYBRID PROGRAM

The hybrid computer program HIXM has successfully solved the equations for the fixed-bed ion-exchange process. In comparison with the digital computer solutions, it is fast and stable. While the accuracy is less, it is still sufficient either for design or correlation purposes.

The time to generate the breakthrough curves up to 100 transfer units for a typical plot such as Graph 8-1 can be allocated as follows:-

Setting up		
Initial potentiometer settings (50)	40	seconds
Three step-size changes, each 25 pots	60	seconds
Computation		
Sweep time (100 points, .05 sec/points)	5	seconds
Computing time, 17 sweeps	85	seconds
Display		
Storage scope, ½ seconds/sweep	9	seconds
Paper tape punch, 1½ seconds/sweep	25	seconds
XY plotter (rarely used) 20 seconds/sweep	400	seconds,

for a total time of 220 seconds. However, it is shown in the next chapter that the computation time per point could easily be reduced to 0.002 seconds, reducing the computing time to 3½ seconds and the total time to 140 seconds. Further reduction in the computing time is superfluous.

Equivalent digital computer times using the IBM 360/44 are 276 seconds for IXLR or 1641 seconds for IXM to a similar accuracy. The

considerable hybrid speed advantages over IXM are even greater if a comparison be made at low values of the mechanism parameter.

The preparation of the hybrid computer to run the ion exchange simulation is greater than if a pure digital computer method were used. On the other hand, the reduction of the system equations to a method of solution is much less of a problem, but program debugging and verification were found to be lengthy for the particular configuration used, especially as adequate interface software had not been developed.

Hybrid computers are much less standarised than digital computers and consequently their programs are very machine-dependent and less transportable. Further, the work required to reinstate a fully-proven and fully-documented hybrid computer program which has not been used for a period (and probably unpatched) is a considerable proportion of the original effort.

In addition, most digital computers large enough for this simulation are not operated by the programmer whereas almost all hybrid computers are "hands-on". Not only is this time consuming, but also it contributes significantly to the frequency of machine malfunctions with the greater difficulties of maintaining and calibrating analog rather than digital equipment. In addition to the usual analog computer verification procedures (initial condition and static check) the use of the "standard" condition run each operating period providing an essential operation and accuracy check.

8-9 CONCLUSION

The hybrid computer model HIXM could be used to simulate the fixed-bed ion exchange process over a wide range of conditions, with advantages in stability and computing speed (but not in accuracy) over the equivalent digital computer model IXM.

Results from HIXM are equivalent to those produced by the less complex digital computer model IXLR which is sufficiently fast and robust to offset some of the hybrid computer advantages, particularly for general design and analysis, as hybrid computers are less common and programs are not readily transported between them.

APPENDIX 8A

Complement of the EAI-590 Computer System.

Digital Computer

Core - 8192(later 16384) 16 bit words

- 1.65micro second access time

Hardware multiply-divide instructions

ASR33 Teletype

64K word disc

High-speed paper-tape reader/punch

Tektronix 611 storage scope

Analog Computer

12 Dual amplifiers

4 Quad amplifiers

6 Dual integrator networks

3 Dual multipliers

50 Sevro-set potentiometers

10 Manual potentiometers

2 Quad log units

2 Manual diode function generators

8 Comparators

8 Function relays

4 Track/store units

8 Digital switches

24 Two-input AND gates

8 Four-input AND gates

4 General registers

4 Decade counters

6 Differentiators

Interface

16 Analog to digital convertors,12 bit + sign

6 Digital to analog convertors,10 or 14 bit + sign

4 Control lines

4 Sense lines

2 Interupt lines

APPENDIX 8B

THE ANALOG PROGRAMMING FOR HIXM

The analog programming for each of the sections of Figure 8-1 can be separately developed, and together give the total analog computer diagram, Figure 8B-1, with the potentiometer setting list, Table 8B-1.

8B-1 The Solution Mass Balance

The equations for each cell are:-

$$\left.\frac{d\bar{y}}{dT}\right|_{N+\Delta N} = -\frac{1}{2\Delta N}\, x_{N+2\Delta N} + \frac{1}{2\Delta N}\, x_N$$

$$\left.\frac{d\bar{y}}{dT}\right|_{N+2\Delta N} = -\frac{3}{2\Delta N}\, x_{N+2\Delta N} + \frac{2}{\Delta N}\, x_{N+\Delta N} - \frac{1}{2\Delta N}\, x_N$$

and are programmed as Figure 8B-2. The scaling is such that the step-size ΔN must be greater than 0.5, which is in accord with the values required for stability and convergence.

The gains G1 and G2 are provided to control the time-scale factor for the analog solution (Section 8B-6) with an extra gain of 10 controlled by the logic signal, BIGB.

8B-2 Integration of the Particle Rate Equations

Figure 8B-3 shows the programming for the integration for the particle concentrations. The equations are:-

$$\frac{dy_2}{dT} = B\left(\frac{32\sigma}{15}\, y_3 - \frac{32\sigma}{15}\, y_2\right)$$

$$\frac{dy_3}{dT} = B\left(\frac{8\sigma}{5}\, y_4 - \frac{32\sigma}{15}\, y_3 + \frac{8\sigma}{15}\, y_2\right)$$

$$\frac{dy_4}{dT} = B\left(\frac{64\sigma}{45}\, y_5 - \frac{32\sigma}{15}\, y_4 + \frac{32}{45}\, y_3\right)$$

where B is the problem time-scale factor, used to relate the speed of the analog solution with the independent problem variable (section 8B-6). To allow a wider range of B values, a logic signal BIGB was used to

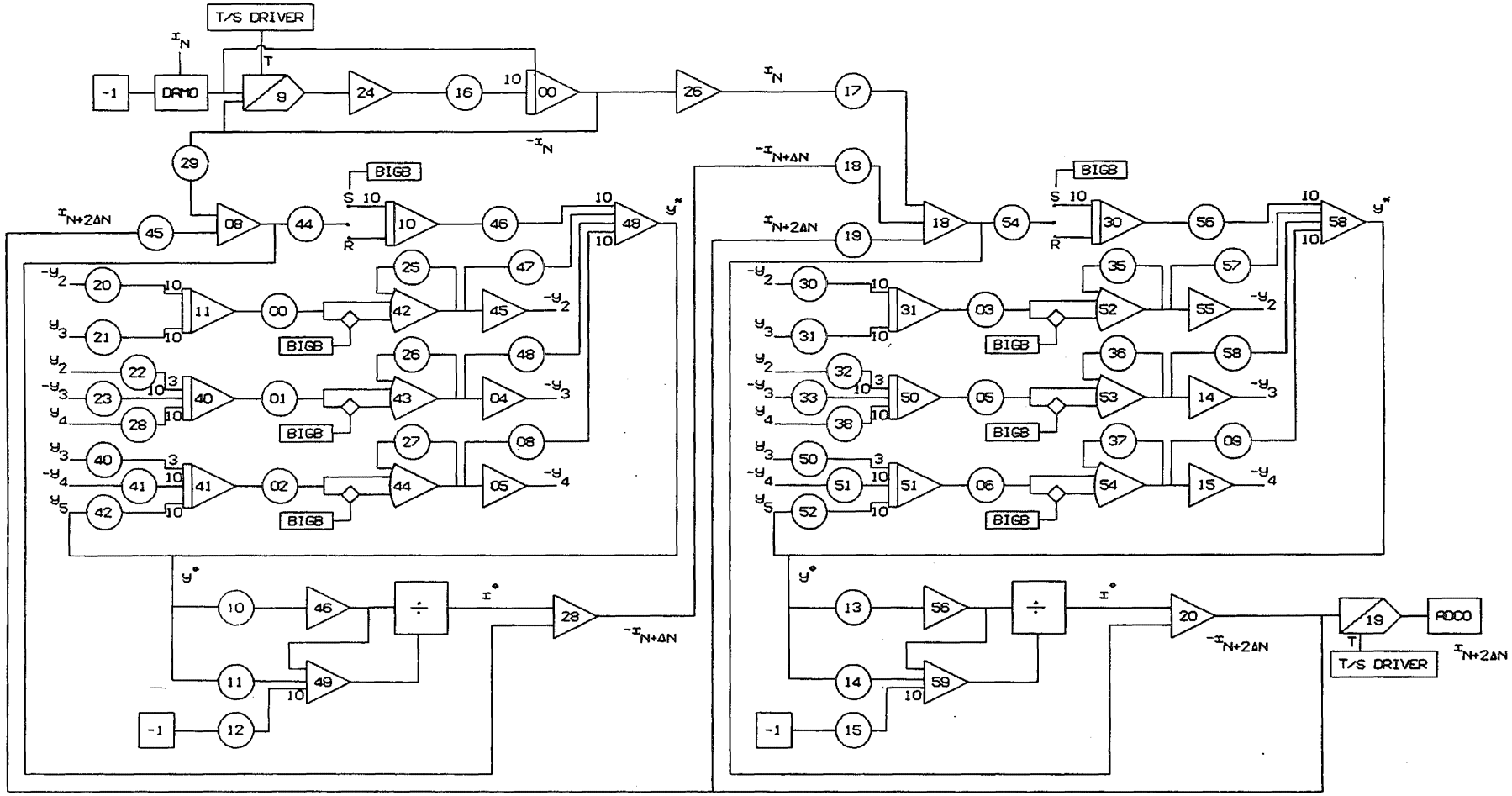


FIGURE 8B-1. ANALOG COMPUTER PROGRAMMING FOR HIXM.

Potentiometer Number	0	1	2	3	4	5	6	7	8	9
00	0.95	0.95	0.95	0.95	-	0.95	0.95	-	0.225	0.225
10	$\frac{G}{K}$	G	$\frac{G}{10}$	$\frac{G}{K}$	G	$\frac{G}{10}$	$\frac{CTSF}{10\ MST}$	$\frac{1}{2\Delta N}$	$\frac{.2}{\Delta N}$	$\frac{.15}{\Delta N}$
20	$\frac{32}{150}$ B	$\frac{32}{150}$ B	$\frac{8}{45}$ B	$\frac{32}{150}$ B	$\frac{1}{\rho}$	$\frac{.95}{\sigma}$	$\frac{.95}{\sigma}$	$\frac{.95}{\sigma}$	.16 B	$\frac{1}{2\Delta N}$
30	$\frac{32}{150}$ B	$\frac{32}{150}$ B	$\frac{8}{45}$ B	$\frac{32}{150}$ B	$\frac{1}{\rho}$	$\frac{.95}{\sigma}$	$\frac{.95}{\sigma}$	$\frac{.95}{\sigma}$	.16 B	-
40	$\frac{32}{135}$ B	$\frac{32}{150}$ B	$\frac{64}{450}$ B	-	G1	$\frac{1}{2\Delta N}$	.4G2	0.25	0.5	-
50	$\frac{32}{135}$ B	$\frac{32}{150}$ B	$\frac{64}{450}$ B	-	G1	-	.4G2	0.25	0.5	-

TABLE 8B-1. Potentiometer settings for the hybrid computer model HIXM.

provide an optional gain of two.

The value of σ is always greater than or equal to one, and this extra gain was provided in the amplifier feedback loop. The factor 0.95 was introduced so that the feedback potentiometer was not required to be set to 0.9999, impossible because of potentiometer loading causing a major source of error.

8B-3 The Particle Mass Balance

The particle mass balance is used in the integral form for four radial elements (Eqn 7-11) to provide the interfacial concentration:-

$$y^* = y_5 = 4\bar{y} - \frac{1}{4}y_2 - \frac{1}{2}y_3 - \frac{9}{4}y_4$$

8B-4 The Equilibrium Relation

The value of x* is calculated from Eqn 8-5:

$$x^* = \frac{\frac{G}{K}y^*}{G(1 - y^*) + \frac{G}{K}y^*}$$

with $G = 1$ for $K > 1$

$G = K$ for $K < 1$

As Figure 8B-5 shows, this equation allows an implementation equilibrium relation to be used for all non-negative values of the separation factor without repatching.

8B-5 The Solution Rate Expression

The new breakthrough curve $x_{N+\Delta N}$ (or $x_{N+2\Delta N}$) is simply calculated from Eqn 8-6 as shown in Figure 8B-6. There is no scaling problem because ρ is always greater than or equal to 1.0.

8B-6 Time-Scaling

The breakthrough curve $x_n(T)$ is a function of the characteristic time, which is analogous to time in the analog simulation. This function is stored in the digital computer as discrete values at equally-spaced points, DELT apart. These points correspond to samples taken at the analog at equal intervals, the micro-sweep time, MST. Time-scaling is fixed by the relation between the characteristic time T and the analog computer time variable t, expressed in terms of DELT and MST.

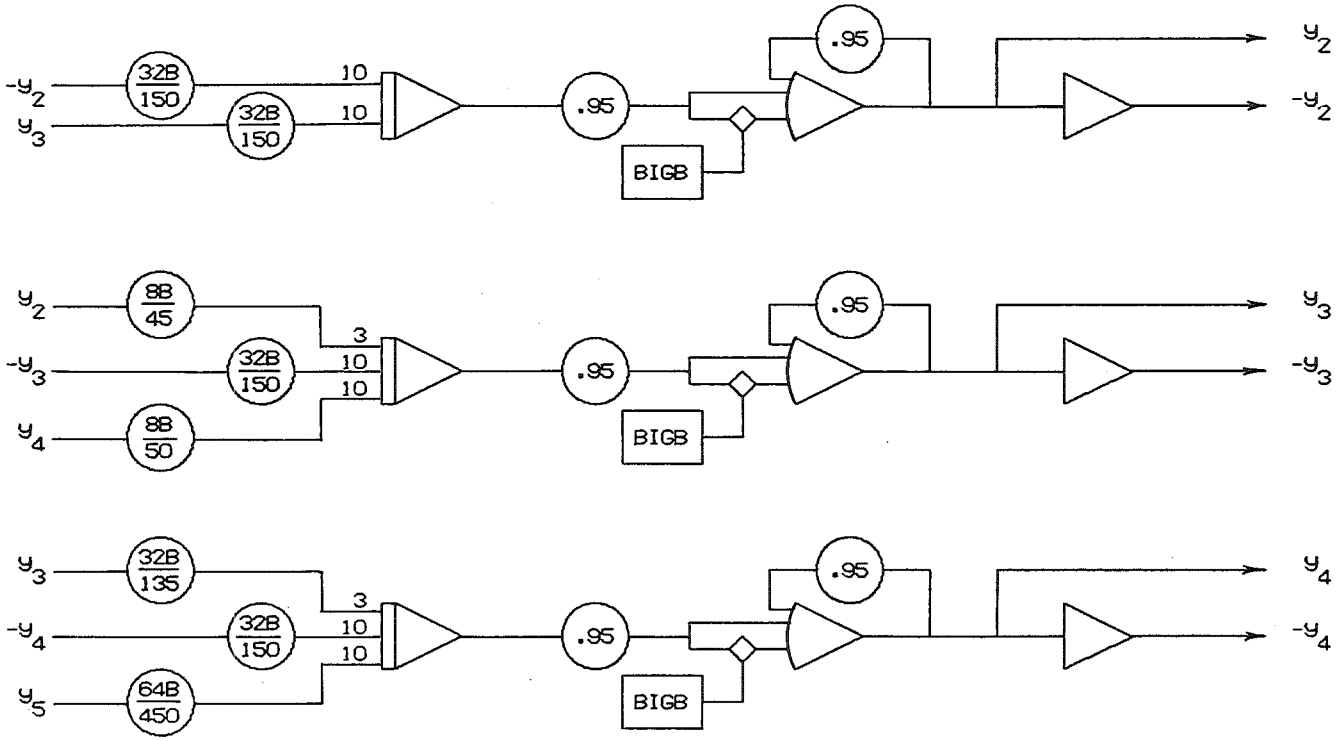
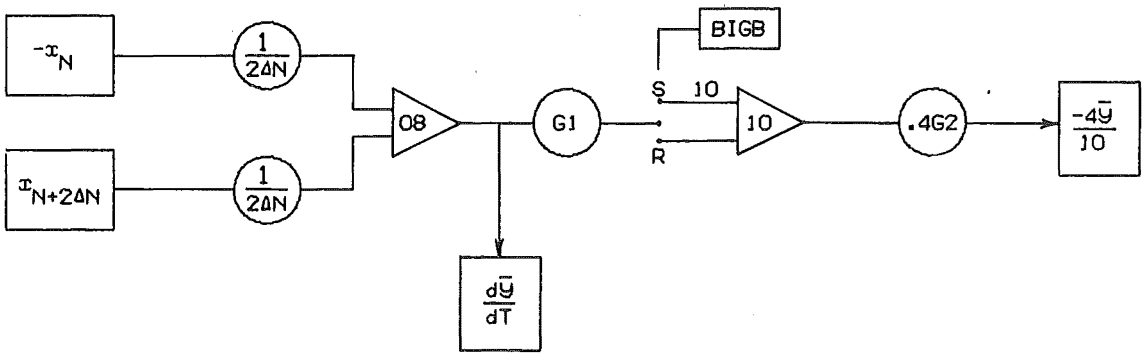


FIGURE 8B-3. ANALOG PROGRAMMING - PARTICLE RATE EQUATION.

FIRST CELL



SECOND CELL

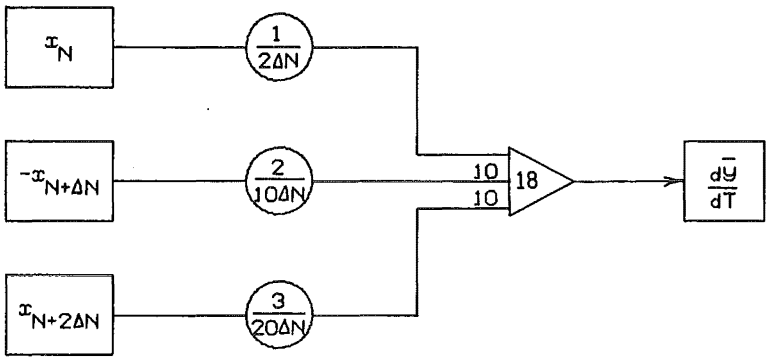


FIGURE 8B-2. ANALOG PROGRAMMING - SOLUTION MASS BALANCE.

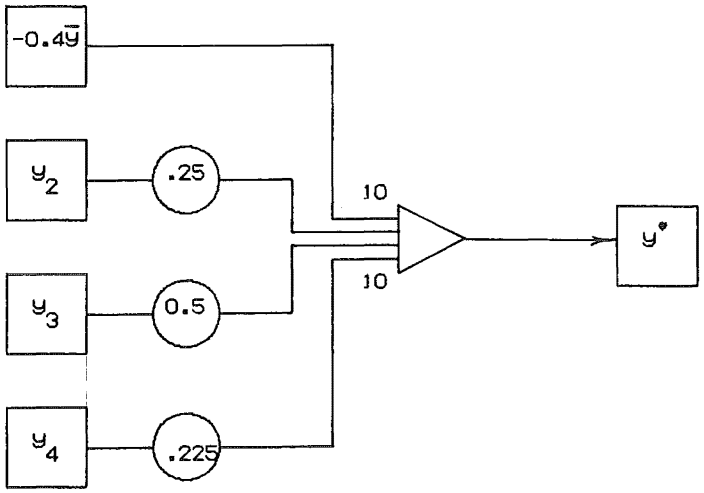


FIGURE 8B-4. ANALOG PROGRAMMING - PARTICLE MASS BALANCE.

When generating complete breakthrough curves, it is convenient to increase the step-size DELT as computation proceeds further down the column. The micro-sweep time is fixed by the time required to pass the required information between the two computers and for the digital computer to update the stored profile, and has been taken as 50 msec for this chapter. The number of sample points NPNT was also held constant. Figure 8B-7 shows some of these relations with the step-size having been doubled three times.

The problem time-scale factor, B, is defined:-

$$B = \frac{\text{Problem rate, characteristic time units/time}}{\text{Analog rate, units/time}}$$

$$= \frac{\text{DELT/MST}}{\text{1.0/ITSF}} = \frac{\text{DELT * ITSF}}{\text{MST}}$$

where ITSF is the integrator time-scale factor (ITSF = R*C where R,C are the resistance, capacitance values used in the integrator). This factor B is included as an extra gain to each integrator.

The characteristic time attained in each sweep is (NPNT + 1)*DELT. Therefore as the step-size in T is increased, the problem time-scale factor must be increased, and the sweep continues to increased values of the characteristic time.

Typically, DELT increased from 0.25 doubling three times to 2.0, the range of values of B required (an 8-fold increase) caused scaling problems in that the range of B values for reasonable settings on the pre-integrator potentiometers is limited. However, the integrator time-scale factors to the y_i integrators could be selected at either 0.1 or 1.0 seconds, and the gains made either 1.0 or 2.0, both under control of logic signals from the digital computer, to give the required flexibility. The conditions used are summarised in Table 8B-2.

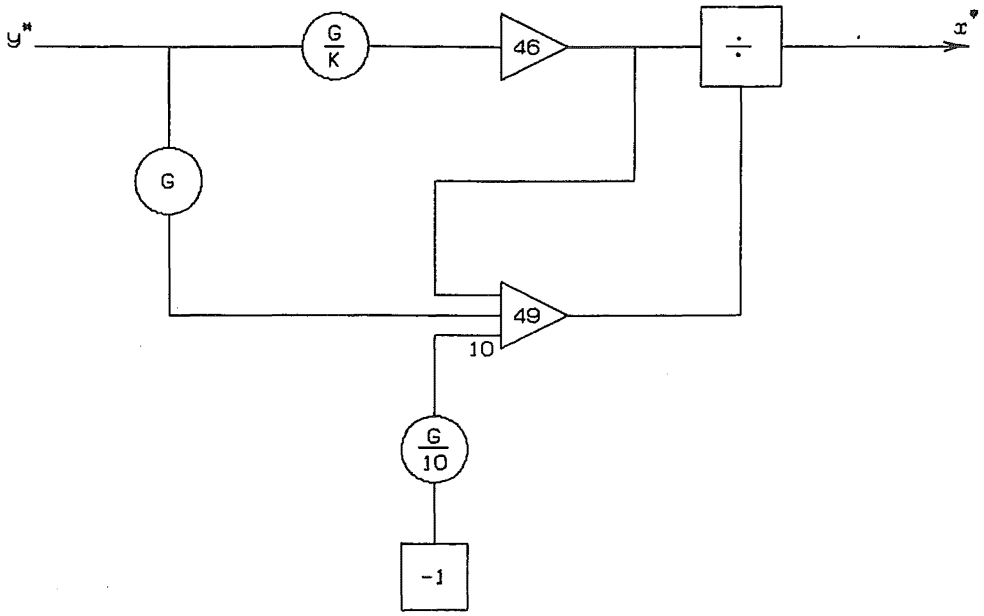


FIGURE 8B-5. ANALOG PROGRAMMING - EQUILIBRIUM RELATION.

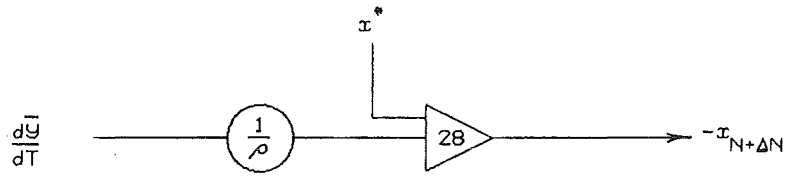


FIGURE 8B-6. ANALOG PROGRAMMING - SOLUTION RATE EQUATION.

DELT	ITSF $\bar{y}$	ITSF y_i	BIGB	B Calculated	B Set	G1	G2
0.25	0.1 sec	1.0 sec	FALSE	5.0	5.0	0.5	1.0
0.5	0.1	0.1	FALSE	1.0	1.0	1.0	1.0
1.0	0.1	0.1	FALSE	2.0	2.0	1.0	2.0
2.0	0.1	0.1	TRUE	4.0	2.0	0.2	2.0

Note:- G1 × G2 × Integrator gain = B

TABLE 8B-2 Problem time-scale factors for the hybrid computer model HIXM.

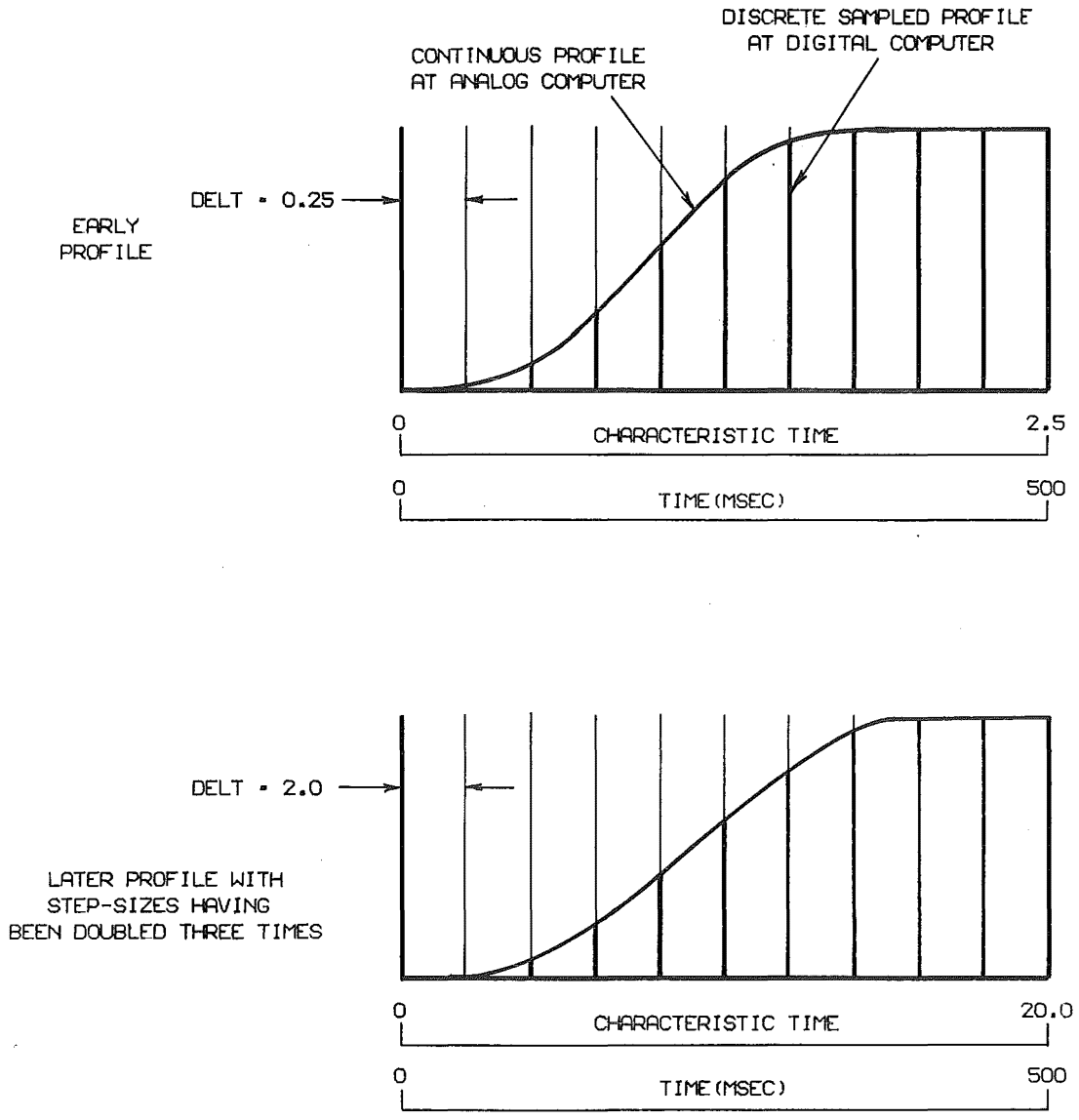


FIGURE 8B-7. SAMPLING OF BREAKTHROUGH CURVE AS STEP-SIZE IS RE-DOUBLED.

SAMPLING AND INTERPOLATION

Sampling and interpolation were controlled by a logic signal, TRACK, which was a series of pulses 100μsec wide occurring every MST seconds (for this chapter, MST = 0.05 seconds).

The circuit used to generate this pulse train is Figure 8C-1. The digital clock produced NPLS pulses/second. The two counters (set to a product NCNT) reduce the pulse rate to NPLS/NCNT per second, i.e.

$$MST = \frac{NCNT}{NPLS}$$

and each pulse is 1/NPLS seconds wide.

With each TRACK pulse, a flip-flop (FF11) was set. During a sweep the digital computer in the SWEEP subprogram (Figure 8-4) remained in a wait loop until a sense line SLOO became high. It responded by resetting the flip-flop with the control line CLOO and transferring the required information. Finally the control line was reset. The time from the TRACK signal until CLOO was again low was 750 ± 100 μsec.

The circuits used for interpolation and sampling are shown in Figure 8C-2 and a timing diagram in Figure 8C-3.

At the start of a sweep to calculate the profile $x_{N+2\Delta N}(T)$ from $x_n(T)$, the analog computer was in the initial condition mode with the digital-to-analog multiplying converter DAMO set to $x_N(1)$. The output of the integrator was $x_N(1)$. The computer was momentarily placed in the HOLD mode and $x_N(2)$ set on DAMO. The sweep commenced with the analog switched to the OPERATE mode. Since the TRACK signal remains momentarily high, the track/store unit has tracked $x_N(2) - x_N(1)$. This constant value (the output from T/S 9 will not change until TRACK is again high) was integrated over the period of time MST and the output from the interpolation circuit increased from $x_N(1)$ to $x_N(1) + [x_N(2) - x_N(1)]$. Linear interpolation between the sample points continued for all the points of the sweep. The system has self-regulation, in that if the output drifts a little low then the difference at T/S 9 will be a little high to correct the error.

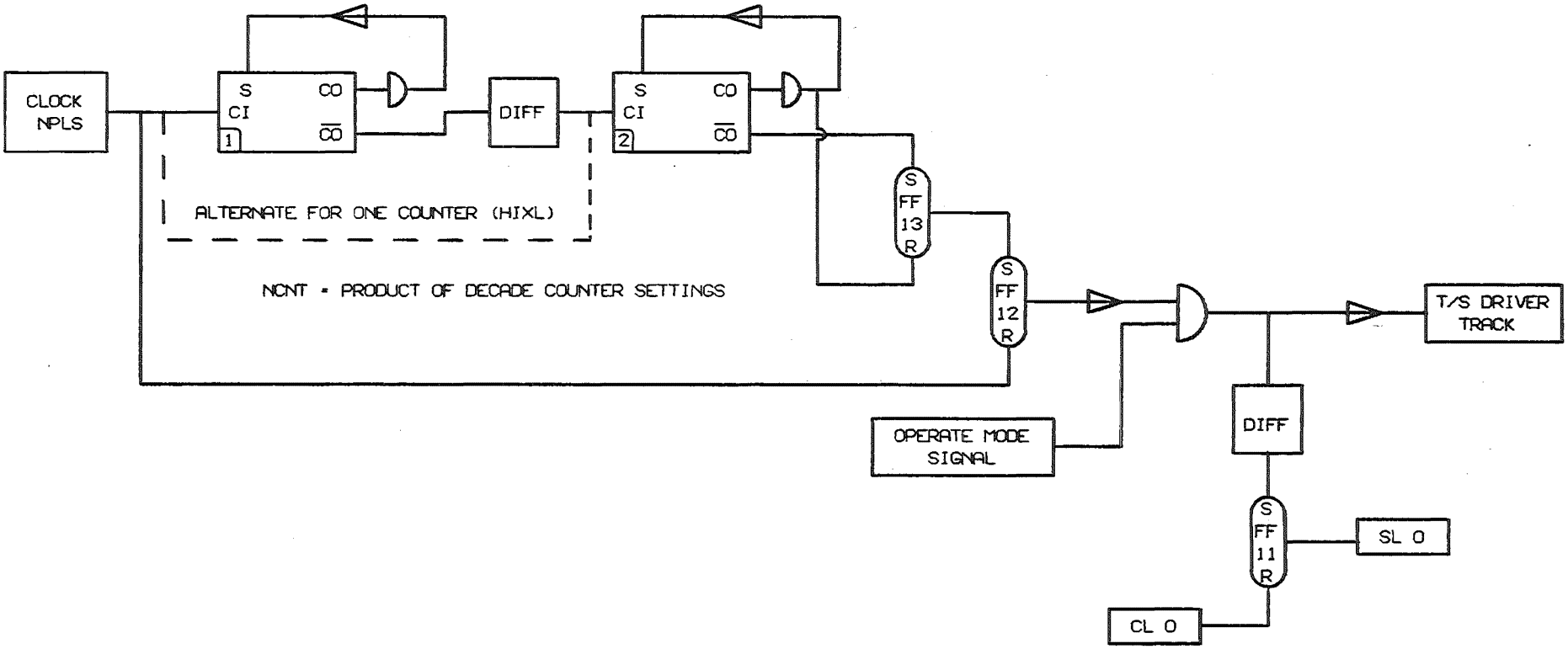
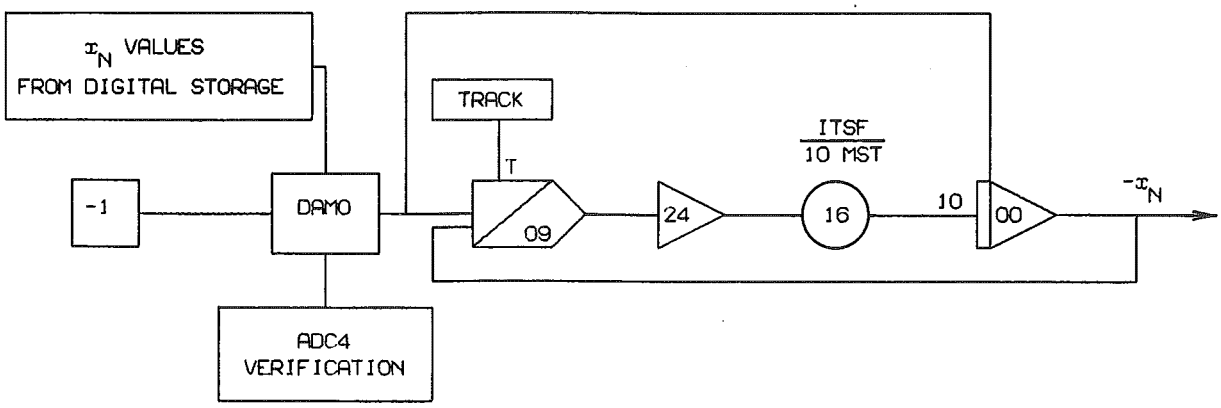


FIGURE 8C-1. ANALOG LOGIC GENERATION OF TIMING SIGNAL, TRACK.

INTERPOLATION



SAMPLING

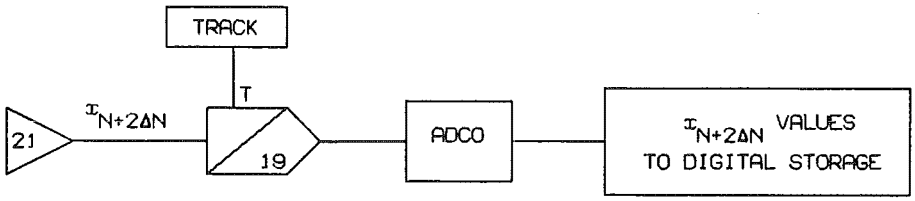


FIGURE 8C-2. ANALOG PROGRAMMING FOR SAMPLING AND INTERPOLATION.

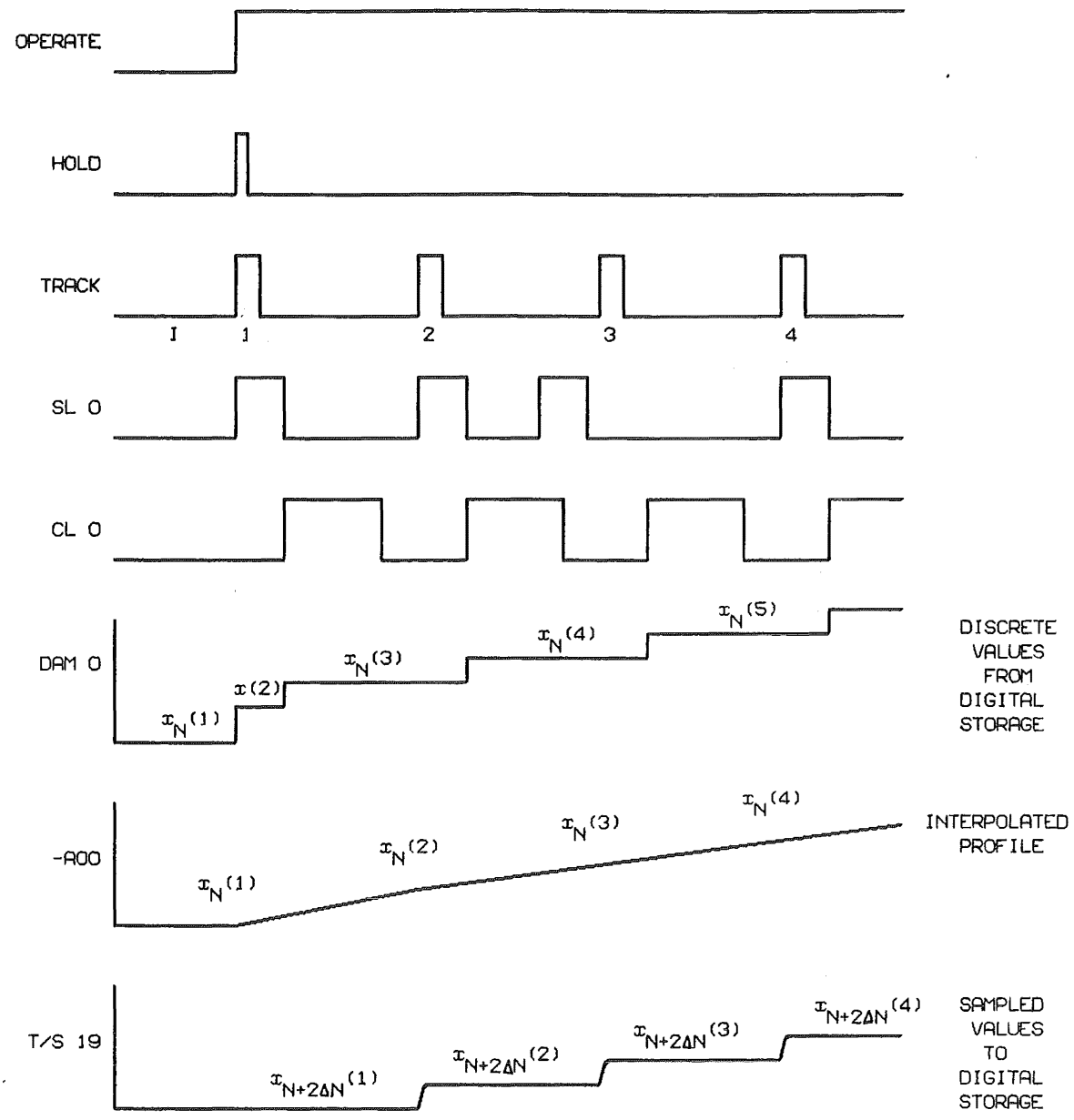


FIGURE 8C-3. TIMING DIAGRAM FOR INTERPOLATION AND SAMPLING.

Figure 8C-2 also shows the simple sampling circuit. At each TRACK pulse the track/store unit T/S 19 sampled the value of $x_{N+2\Delta N}$ at this instant and stored it during the next microsweep time, sufficient for the digital computer to read the value from the analog to digital converter ADCO several times for verification.

APPENDIX 8D

```
C
C     MAINLINE HYBRID IXM PROGRAM
C
C    PURPOSE
C
C      TO SIMULATE FIXED BED ION EXCHANGE COLUMN BEHAVIOUR
C
C    I/O SUBPROGRAMS REQUIRED
C
C      PNCH44   TO PUNCH RESULTS ON PAPER TAPE IN A FORM ACCEPTABLE
C               TO THE IBM 360/44 COMPUTER FOR PLOTTING
C      READI    TO READ AN INTEGER
C      TYPEH    T O TYPE AN ALPHAMERIC RECORD
C      TYPEI    TO TYPE AN INTEGER
C
C    INTERFACE SUBPROGRAMS REQUIRED
C
C      FIXIT    TO DISPLAY A LINE
C      MODE     TO SELECT AN ANALOG COMPUTER MODE
C      POT1,POT2,POT3
C               TO SET GROUPS OF POTENTIOMETERS
C      RD580    TO READ ANALOG COMPUTER COMPONENT VALUES
C      SDAM     TO SET A MULTIPLYING A/D CONVERTER
C      SWGOUT   TO INITIALISE DISPLAY ROUTINES
C      SWEEP    TO COMPUTE A SINGLE ANALOG COMPUTER SWEEP
C      SCOPE    TO DISPLAY A COMPUTED BREAKTHROUGH CURVE
C
       COMMON L2,L3
       SCALED FRACTION A(202)
       SCALED FRACTION AP(101)
       DIMENSION IGO(3)
       LOGICAL L2,L3
       DIMENSION IA(205)
       SCALED FRACTION V
       REAL NOJT
       LOGICAL OUTPUT,LO,HI
       REAL N,K,NMAX
       INTEGER FLAG
       LOGICAL PNCH
       LOGICAL SENSW
       DATA LO,HI/.FALSE.,.TRUE./
       DATA IGO(1),IGO(2),IGO(3)/'215,'212,'337/
       DATA IDATE/0/
C
C      INITIALISE CONSOLE AND VALUES
       S=.9999
       FLAG=16383
C
C      READ CALCULATION VALUES
C
       IA(6)=1000
       IA(2)=1000
       IA(3)=1000
       IA(5)=IDATE
       I=4000
```

```
      IA(4)=250
      J=2000
      NPLS=10000
      NCNT=500
      NPNT=100
    1 CALL TYPEH(IGO,3)
C     READ DATE,1000K,1000ZETA:::::::::::::::
      CALL READI(10,IA(5),IA(6),IA(2))
      IDATE=IA(5)
      Z=IA(6)
      K=Z/1000.
      Z=IA(2)
      ZETA=Z/1000.
      CALL TYPEH(IGO,3)
C     READ 1000(DELN,DELNMX,DELT,DELTMX)::::::::
      CALL READI(10,IA(3),I,IA(4),J)
      Z=IA(3)
      DELN1=Z/1000.
      Z=I
      DELNMX=Z/1000.
      Z=IA(4)
      DELT1=Z/1000.
      Z=J
      DELTMX=Z/1000.
      CALL TYPEH(IGO,3)
      CALL READI(10,NPLS,NCNT,NPNT)
C
C     EMST IS THE REAL TIME IN SECONDS FOR A MICROSWEEP
C     TS IS THE TIME IN SECONDS FOR A FULL SWEEP
C
C      SENSW1 FOR 0.1SEC INTEGRATOR TIME SCALE FACTOR

C      SENSW2 TO PUNCH OUTPUT RESULTS
C      SENSW3 TO READ A FOR ARBITARY BOUNDARY CONDITIONS
C     SENSW4 TO DRAW BOX FOR DISPLAY ALIGNMENT
     SENSW8 TO DISPLAY
C
   77 IF(.NOT.SENSW(8))GOTO3
      CALL SWGOUT
      CALL FIXIT(100,900,1)
      CALL FIXIT(600,900,0)
      CALL FIXIT(600,100,0)
      CALL FIXIT(100,100,0)
      CALL FIXIT(100,900,0)
      IF(SENSW(4))GOTO77
    3 PNCH=.FALSE.
      NH1=NPNT/2+1
      NH2=NH1+1
      L2=LO
      L3=LO
      CALL SCL (LO,LO,L2,L3)
      DELN=DELN1
      DELT=DELT1
      IF(SENSW(2))PNCH=.TRUE.
      IF(.NOT.PNCH)GOTO27
      IA(1)=FLAG
```

```
      IA(7)=NPLS
      IA(8)=NCNT
      IA(9)=NPNT
      J=-9
      CALL PNCH44(IA,J)
   27 CONTINUE
      Z=NCNT
      Y=NPLS
      EMST=Z/Y
      Y=NPNT
      TS=Y*EMST
      NPNT1=NPNT+1
      NPNT2=NPNT1+1
      NPNT3=NPNT2+1
C
C     GET RO,SIGMA
C      IF ZETA=0.0,PUT RO=-10.0
C
      RO=1.
      SIGMA=ZETA
      IF(ZETA.GT.1.)GOTO6
      RO=-10.0
      SIGMA=1.
      IF(ZETA.GT.0.0001)RO=1.0/ZETA
C
C     SET ALL POTENTIOMETERS
C
    6 CALL POT1(EMST,K,RO,SIGMA)
      CALL POT2(EMST,DELT)
      CALL POT3(DELN)
      IPOP=1
      IF(.NOT.PNCH)GOTO2
    7 CONTINUE
C
C     READ AND PUNCH POTENTIOMETER VALUES
C
      CALL RD580(1,AP)
      IA(1)=16382
      DO382I=2,62
      DUM=AP(I-1)
      IA(I)=DUM*10000.
  382 CONTINUE
      J=-61
      CALL PNCH44(IA,J)
      IF(IPOP.EQ.2)GOTO9
      V=W
      CALL SDAM(0,V)
      CALL MODE('3000)
      DO210I=1,60
  210 A(I)=0.05
C
C     READ AND PUNCH ALL AMPLIFIER VALUES IN RESET FOR INITIAL
C      CONDITION CHECK
C
      CALL RD580(2,A)
```

```
      IA(1)=16381
      DO381I=2,62
      DUM=A(I-1)
      IA(I)=DUM*1000.
      IF(DUM.LT.0.0)IA(I)=-IA(I)+1000
  381 CONTINUE
      J=-61
      CALL PNCH44(IA,J)
C
C     INITIALISE FIRST PROFILE TO REQUIRED BOUNDARY CONDITION
C
    2 DO202I=1,NPNT1
  202 A(I)=W
      N=0.0
      INIL=0
C    NON-STANDARD INPUT PROFILE?
      IF(.NOT.SENSW(3))GOTO4
C
C     READ T VALUE FOR REGERATION START
      CALL TYPEH(IGO,3)
      CALL READI(10,I)
      TSW=I
C
C     CALCULATE DATA POINT FOR CHANGE
      NSW=TSW/DELT
      IF(NSW.GE.NPNT1)GOTO4
      DO207I=NSW,NPNT1
      A(I)=0.05
  207 CONTINUE
C
C     BEGIN SWEEPS
C
    4 N=N+DELN+DELN
      CALL SWGOUT
      CALL SWEEP(A,NPNT,LO)
C
C     STEP SIZE CHANGE IN N,T REQUIRED?
C
      J=9*NPNT/10
      IF(A(J).GT..99.OR.DELT.GT..6*DELTMX)GOTO17
      IF(DELN.GT..6*DELNMX)GOTO8
C
C     DOUBLE STEP SIZE DOWN COLUMN
C
      DELN=DELN+DELN
      CALL POT3(DELN)
C
C     DOUBLE STEP SIZE DOWN PROFILE
C
    8 DELT=DELT+DELT
      CALL POT2(EMST,DELT)
C
C     DUMP POT VALUES
C
      IPOP=2
      IF(PNCH)GOTO7
```

```
    9 CONTINUE
      DO204I=1,NH1
      A(I)=A(2*I-1)
  204 CONTINUE
      NSW=TSW/DELT
      DO205I=NH2,NPNT1
      A(I)=.9999S
      IF(SENSW(3).AND.I.GE.NSW)A(I)=0.0S
  205 CONTINUE
C
C     PREPARE ARRAY FOR PUNCHING AND DISPLAY
C
   17 DO203I=1,NPNT1
      F=A(I)
      IF(F.LT.0.0)F=0.0
      IA(I)=F*10000.0+0.5
  203 CONTINUE
C
C     PUNCH OR DISPLAY LAST PROFILE
C
   24 FAC=800.0*DELT/Y/DELTMX
      IF(SENSW(8))CALL SCOPE(IA,FAC,NPNT1)
      IF(.NOT.PNCH)GOTO4
      IA(NPNT2)=100.0*N
      IA(NPNT3)=1000.0*DELT
      J=-NPNT3
      CALL PNCH44(IA,J)
      GOTO4
      END
```

```
      SUBROUTINE SWEEP(A,NPNT)
C
C     PURPOSE
C
C       TO CONTROL THE ANALOG COMPUTER FOR A SINGLE SWEEP, TAKING
C       THE PROFILE AT N AND COMPUTING ITS REPLACEMENT AT N+2*DELN
C
C
C     USAGE
C
C       CALL SWEEP(A,NPNT,OUTPUT)
C
C     ARGUMENTS
C
C       A       THE INPUT AND OUTPUT PROFILE
C                 -SCALED FRACTION
C
C       NPNT    THE NUMBER OF POINTS
C                 -INTEGER
C
C       OUTPUT NOT USED IN SWEEP, BUT INCLUDED TO CORRECTLY SET
C              CONTROL LINES
C
C     SUB-PROGRAMS REQUIRED
C
C       DELAY    TO DELAY THE DIGITAL COMPUTER FOR A PERIOD GIVEN
C                BY THE ARGUMENT IN MILLISECONDS
C       MODE     TO SELECT AN ANALOG COMPUTER MODE
C       RSADC    TO SELECT AND READ AN A/D CONVERTER
C       RSL      TO READ A SENSE LINE
C       RVADC    TO READ AND VERIFY A PREVIOUSLY SELECTED A/D
C                CONVERTER
C       SCL      TO SET ALL CONTROL LINES
C       SDAM     TO SET A MULTIPLYING D/A CONVERTER
C       TYPEI    TO TYPE AN INTEGER
C
C
      LOGICAL L2,L3
      SCALED FRACTION A(1),V1,V2
      SCALED FRACTION V
      LOGICAL SL,HI,LO,OUTPUT
      DATA MSP,MIC,MHD,MOP/'3400,'3000,'2400,'2000/
      DATA HI,LO/.TRUE.,.FALSE./
      NPNT1=NPNT+1
      KURSE=1
C
C       WAIT FOR ANY OVERLOADS TO SUBSIDE
C
    3 CALL RSL(3,SL)
      IF(SL)GOTO3
      IADC=0
      CALL RSADC(IADC,V)
      CALL MODE(MIC)
      V=A(1)
```

```
      CALL SDAM(0,V)
      CALL DELAY(300)
      CALL MODE(MHD)
      V=A(2)
      CALL SDAM(0,V)
      CALL MODE(MOP)
      DO200I=2,NPNT
      I1=I-1
      V=A(I+1)
C
C     WAIT FOR SENSE LINE 0 TO GO HIGH
C
    2 CALL RSL(0,SL)
      IF(.NOT.SL)GOTO2
C
C     SET CONTROL LINE 0 HIGH TO INDICATE DIGITAL COMPUTER WORKING
C
      CALL SCL(HI,OUTPUT,L2,L3)
C
C     SET AND CHECK DAM
C
    7 CALL SDAM(0,V)
      CALL RSADC(4,V1)
C     CONTINUE IF DAM SET WITHIN 0.0005
      P=V-V1
      IF(ABS(P).LT.0.0010)GOTO8
      KURSE=KURSE+1
      IF(KURSE.GT.5)CALL TYPEI(7,KURSE)
      GOTO7
C
C     READ AND VERIFY ADC
C
    8 CALL RSADC(IADC,V)
      CALL RVADC(V)
C
C     END OF DIGITAL ACTION
C
     CALL SCL(LO,OUTPUT,L2,L3)
C
C     JPDATE PROFILE
C
      A(I1)=V
  200 CONTINUE
      CALL MODE(MHD)
      IF(KURSE.GT.1)CALL TYPEI(7,KURSE)
      CALL MODE(MSP)
      RETURN
      END
```

THE AXIAL DISPERSION MODEL (HIXL)
- HYBRID COMPUTER SOLUTION

Axial dispersion is normally negligible in conventional strong acid-strong base ion exchange column operations, but can be significant for other sorption (or thermal) fixed-bed processes, particularly with gases rather than liquids or with low flow rates through the column.

This chapter extends the hybrid treatment to include an extra term in the solution mass balance to account for axial dispersion. The modifications required to expand HIXM to HIXL for some, rather than dominant, axial dispersion appeared minor. However, accuracy difficulties arose because the method of solution did not integrate along the natural characteristics of the system and because the derivative form of the particle mass balance had to be used. Particular attention to the performance and programming of the analog computer was necessary before satisfactory computed results were obtained. These have been used to extend the Vermeulen-Hiester-Thomas reaction kinetic design method to include axial dispersion effects.

9-1 AXIAL DISPERSION

The dispersion mechanisms in previous chapters have been limited to equilibrium effects and to diffusional resistance to mass transfer, both within the particle and in the surrounding solution film.

In addition, there are other effects which can contribute to axial dispersion:-

(a) molecular diffusion of solute down the column due to concentration gradients established by the fact of adsorption

(b) the mixing of fluid in the interstices between particles

(c) the formation of uneven velocity profiles within the column due to non-uniformity in the packed bed.

These effects can be characterised (Lightfoot et al., 1962) by an effective axial diffusivity, E_A, within an additional dispersive term in the solution mass balance (Eqn 2-10):-

Source	Physical Form	
Solution mass balance, Eqn 2-10.	$E_A \frac{\partial^2 x}{\partial z^2} = v\frac{\partial x}{\partial z} + \frac{\partial x}{\partial t} + D_R \frac{\partial \bar{y}}{\partial t}$	(9-1)
Particle mass balance, Eqn 2-13.	$\frac{\partial \bar{y}}{\partial t} = \frac{6D_p}{d_p} \left.\frac{\partial y}{\partial r}\right\|_{r= d_p/2}$	(9-2)
Solution rate, Eqn 2-8.	$\frac{\partial \bar{y}}{\partial t} = k_f(x - x^*)$	(9-3)
Particle rate, Eqn 2-5.	$\frac{\partial y}{\partial t} = D_p(\frac{\partial^2 y}{\partial r^2} + \frac{2}{r}\frac{\partial y}{\partial r})$	(9-4)
Equilibrium expression, Eqn 2-4.	$\frac{y^*}{1 - y^*} = K \frac{x^*}{1 - x^*}$	(9-5)

Nomenclature (additional to Table 7-1)

D_R Distribution ratio, $\frac{Q}{\varepsilon C_o}$.

E_A Effective axial diffusivity (L^2T^{-1})

TABLE 9-1. Equations and nomenclature for the axial dispersion model HIXL.

$$E_A \frac{\partial^2 x}{\partial z^2} = \frac{v}{\varepsilon} \frac{\partial x}{\partial z} + \frac{\partial x}{\partial t} + \frac{Q}{\varepsilon C_o} \frac{\partial \bar{y}}{\partial t} \qquad (9\text{-}1)$$

There is a source of possible confusion in the literature arising from the definition of the axial diffusivity in this equation; some (Lightfoot, 1962; Lapidus, 1952) have used this form, others (Acrivos, 1960; Quilici and Vermeulen, 1969) have taken a value which is the above multiplied by the voidage.

The equations of the model HIXL are listed, with nomenclature, in Table 9-1.

9-2 INITIAL AND BOUNDARY CONDITIONS

These conditions are the same as those for HIXM (Section 7-2) and with the same possibilities for generalisation, except that axial dispersion affects the boundary condition (Section 2-7) which becomes:-

$$x_{z=0} = x_o + \frac{\varepsilon E_A}{v} \cdot \frac{\partial x}{\partial z} \qquad z = 0,\ t > 0 \qquad (9\text{-}6a)$$

where x_o is the concentration history of the solution fed to the top of the column. This will be called the finite bed condition, in contrast to the more tractable infinite bed condition

$$x_{z=0} = x_o \qquad z = 0,\ t > 0 \qquad (9\text{-}6b)$$

so-called because the fixed-bed is considered as a segment of an infinite column of adsorbent.

9-3 PREDICTION OF BREAKTHROUGH CURVES INCLUDING AXIAL DISPERSION

Analytical solutions to the fixed-bed equations including the axial dispersion term have been derived using one or more of the common simplifying assumptions.

By assuming that the bulk phases are in equilibrium, and that this equilibrium is linear (i.e. all widening of the breakthrough curve is due to axial dispersion) Lapidus and Amundson (1952) have derived for an infinite column:-

$$x = \tfrac{1}{2}\{1 + \mathrm{erf}[\frac{vt - \varepsilon z(1 + D_R)}{2\varepsilon\sqrt{E_A(1 + D_R)t}}] + \exp(\frac{vz}{\varepsilon E_A}) \cdot$$

$$\mathrm{erfc}[\frac{vt + \varepsilon z(1 + D_R)}{2\varepsilon\sqrt{E_A(1 + D_R)t}}]\} \qquad (9\text{-}7)$$

where D_R is the distribution ratio, $\frac{Q}{\varepsilon C_o}$. The term containing the complementary error function is negligible for columns of reasonable length (Lightfoot et al., 1962; Babcock et al., 1966) and this expression simplifies to:-

$$x = \tfrac{1}{2}\ \mathrm{erfc}\left[\frac{z - v_F t}{2\sqrt{t\ E_A}}\right] \qquad (9\text{-}8)$$

where v_F is the velocity of the solvent front

$$v_F = \frac{v}{\varepsilon} \cdot \frac{1}{1 + D_R}$$

This equation can be expressed in terms of dimensionless variables

$$x = \tfrac{1}{2}\ \mathrm{erfc}\left[\frac{1 - \tau}{2}\sqrt{\frac{N_L}{\tau(1 + D_R)}}\right]$$

where τ is a dimensionless time parameter

$$\tau = \frac{vt}{(1 + D_R)\varepsilon z}$$

and N_L the number of axial dispersion transfer units:-

$$N_L = \frac{vz}{\varepsilon E_A}$$

defined to correspond to transfer units for film or particle mass transfer resistance.

Lapidus and Amundson (1952) also developed an explicit breakthrough curve for linear equilibrium and film resistance to mass transfer, in addition to the axial dispersion mechanism. Arbitrary initial conditions were included. Van Deemter et al. (1956) have applied this result to gas chromatography and showed that an equivalent dispersion factor could be defined in terms of a linear sum of axial dispersion and mass transfer resistances.

The above results were derived for the infinite bed boundary condition but Bastion and Lapidus (1956) have used the finite bed condition with the assumption of bulk equilibrium. For a relatively short column ($N_L = 6$, $D_R = 24$) there was less than 2% difference in the computed solution concentrations between the two boundary conditions.

The most general solution for linear equilibrium and axial dispersion (Babcock et al., 1966) was an extension of Rosen's analysis

(Section 3-2). Results are not analytical in that they must be obtained from a rather difficult numerical integration. A computer program, called BGP, is detailed in Appendix 9A and has been used to verify in part the various simulations developed in this thesis with equivalent assumptions (IXM and HIXM for no axial dispersion, and HIXL in this chapter, all for linear equilibrium).

Babcock has suggested an approximate solution which is analytical and does not require computer evaluation. This simplified equation is of the same form as Eqn 9-8 with the equivalent axial diffusivity E_A expressed as the sum of terms reflecting the contribution of solid and film diffusion, and of axial diffusion itself. Interesting and useful as this is, it assumes that the infinite integral to be evaluated has converged at sufficiently small values of the variable of integration, λ, that λ^6 is negligible. Experience with this quadrature, described in Appendix 9A, suggests that this is not often true.

Houghton et al. (1960, 1961, 1965, 1966) used digital computer methods to predict the effects of column parameters and operating decisions on chromatographic separations. The fixed-bed equations (including axial dispersion but no mass transfer resistance and with non-linear equilibrium expressed as a second-degree polynomial) were reduced to a second-order parabolic partial differential equation.

The existence of asymptotic solutions for favourable equilibrium has been proved for axial dispersion alone (Lightfoot, 1957) and for additional mass transfer resistance (Cooney and Lightfoot, 1965). Acrivos (1960) has generated constant pattern solutions for film diffusion and axial dispersion, locating the breakthrough curve such that $x = 0.5$ at $z = 1.0$. In addition, Acrivos has shown that the effects of mass transfer resistance and axial dispersion are not additive except for linear or "almost linear" equilibrium.

Quilici and Vermeulen (1969) have tabulated numerical constant-pattern breakthrough curves for axial dispersion and each of the mass transfer mechanisms:-

(a) Film diffusion (Eqn 2-8)

(b) Solid diffusion

(i) linear rate expression (Eqn 2-7)

(ii) quadratic rate expression (Eqn 3-13)

(c) Pore diffusion

(d) Reaction Kinetics (Eqn 3-20)

In each, the breakthrough curve was located by trial and error to satisfy the overall column mass balance (Eqn 2-26). The infinite bed boundary condition was used.

The sorption of non-electrolytes on to fixed beds of ion-exchange resin particles has been studied by Colwell and Dranoff (1969, 1971), and a digital computer simulation developed to assess the important adsorption mechanisms. Their mathematical model included non-linear-equilibrium, axial dispersion and particle diffusion, but differed from HIXL in the equilibrium expression

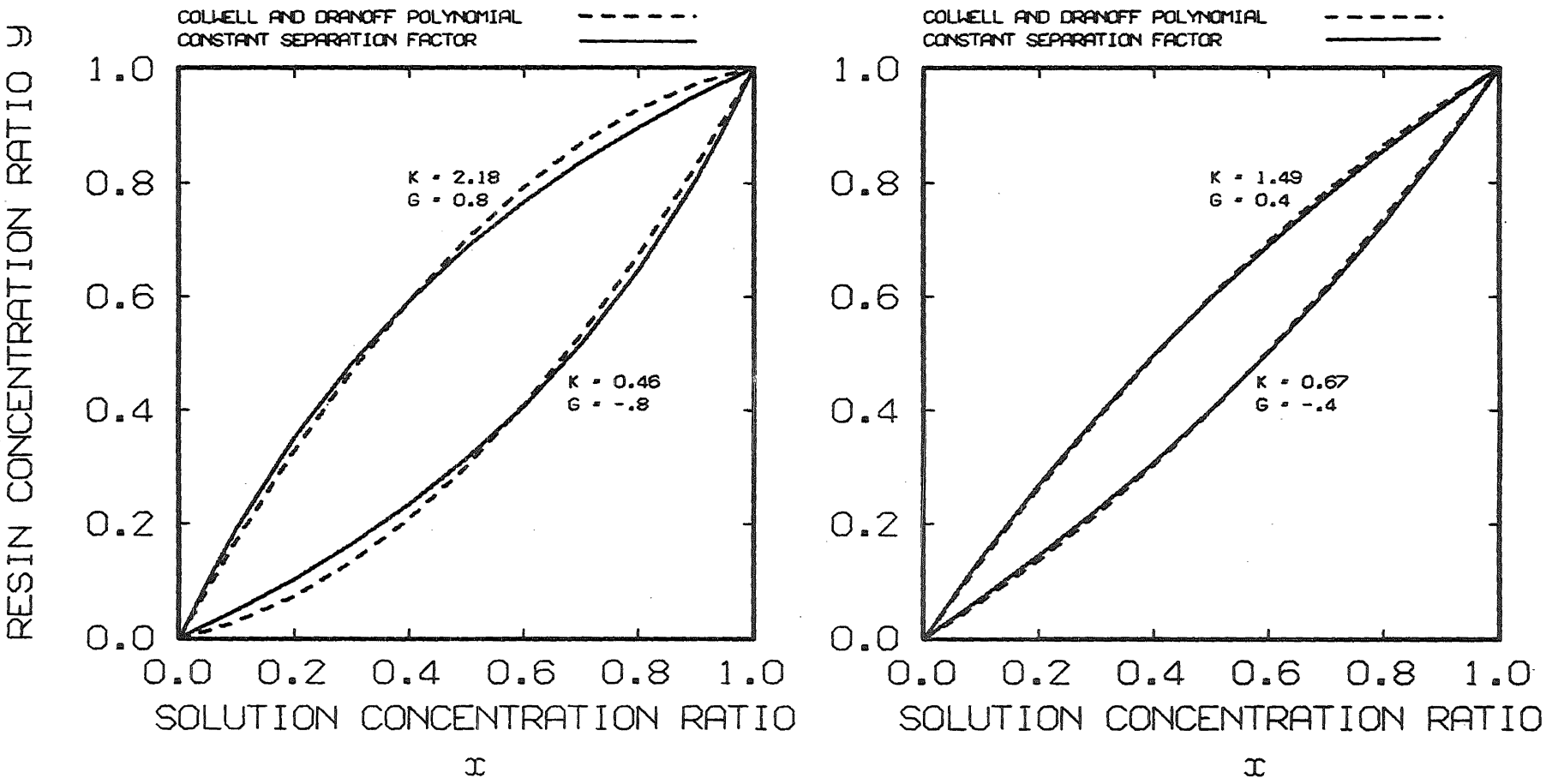
$$y^* = [1 + G(1 - x)]x \qquad (9\text{-}5a)$$

and in that film diffusion was not included (earlier experimental work had shown it insignificant for this system, Colwell and Dranoff, 1966). Graph 9-1 shows that the constant separation factor form (Eqn 9-5) is little different to Eqn 9-5a for "almost linear" equilibrium.

The significant difference between Colwell's simulation and that developed in this thesis is in the method of solving the equations. Colwell and Dranoff followed Rosen's analytical path to reduce the problem to a difficult integro-differential expression. Numerical methods were then used to integrate this equation. This contrasts with the simpler method of this thesis in that numerical methods were applied directly to the normalised differential equations.

The difficulties of solving the fixed-bed equations, particularly with axial dispersion, have resulted in the development of stochastic models of packed bed mixing and mass transfer, such as that of Schmalzer and Hoelscher (1971) who criticise the interpretation of mixing in the interstices of the packing either as a diffusion process or as a series of mixers. Certainly the spread of data in a correlation of Reynolds and Peclet numbers (their Figure 1) casts doubt on the adequacy of axial dispersion theory and experiment.

Experimental dispersion studies have been reviewed by Perkins and



GRAPH 9-1. THE COLWELL AND DRANOFF EQUILIBRIUM EXPRESSION.

Source	General Form	
Solution mass balance	$\theta\frac{\partial^2 x}{\partial N^2} = \frac{\partial x}{\partial N} + \frac{\partial \bar{y}}{\partial S} + \frac{1}{D_R}\frac{\partial x}{\partial S}$	(9-9)
Particle mass balance	$\frac{\partial \bar{y}}{\partial S} = \frac{\sigma}{5}\frac{\partial y}{\partial R}\Big\vert_{R=1}$	(9-10)
Solution rate equation	$\frac{\partial \bar{y}}{\partial S} = \rho(x - x^*)$	(9-11)
Particle rate equation	$\frac{\partial y}{\partial S} = \frac{\sigma}{15}(\frac{\partial^2 y}{\partial R^2} + \frac{2}{R}\frac{\partial y}{\partial R})$	(9-12)
Equilibrium	$\frac{y^*}{1 - y^*} = K\frac{x^*}{1 - x^*}$	(9-13)

Nomenclature (additional to Table 9-1)

N_L The number of axial transfer units, $\frac{vz}{\varepsilon E_A}$

S The shifted characteristic time; either particle phase ($S_p = k_p t$) or solution phase ($S_f = k_f t$).

θ The dispersion parameter, N/N_L.

TABLE 9-2 Equations and nomenclature for the hybrid computer solution HIXL.

Johnson (1963) who explain the considerable difference in behaviour between gas and liquid systems in terms of the large variation in the Schmidt number. Miller and King (1966) compare results from seven studies, and these show considerable variation. Their correlation will predict the particle Peclet number within 25% for linear systems, in the range of Reynolds' number from 10^{-2} to 10^{4}.

9-4 THE EQUATIONS OF HIXL

Similar substitutions to those used in Section 2-9 reduce the equations of Table 9-1 to a form suitable for computation (Appendix 9B). The equations are listed in Table 9-2 and are similar to those of HIXM but the solution mass balance (Eqn 9-9) contains extra terms and the differential particle mass balance (Eqn 2-23b) is used for the first time.

The computation is based, as before, on the side with the smaller number of transfer units. The dispersion parameter:-

$$\theta = \frac{N}{N_L}$$

reflects the importance of axial dispersion in the same way as the mechanism parameter indicates the degree of film diffusion.

The number of axial transfer units is defined to be analogous to N_p or N_f

$$N_L = \frac{vz}{\varepsilon E_A}$$

This dimensionless ratio has sometimes been called the column Peclet number.

The shifted characteristic time:-

$$S = kt$$

is equivalent to the more generally used characteristic time:-

$$T = k(t - \frac{\varepsilon z}{v})$$

where the general mass transfer coefficient, k, is chosen to correspond to the appropriate computational basis. The two are related:-

$$S = kt = T + k \cdot \frac{\varepsilon z}{v} = T + \frac{N}{D_R} \qquad (9\text{-}14)$$

9-5 THE HYBRID COMPUTER SOLUTION

The main differences between the methods of solution for HIXL and HIXM occur in the analog computer programming.

The general method is shown in Figure 9-1. Estimates of the derivatives $\frac{\partial x}{\partial N}$ and $\frac{\partial^2 x}{\partial N^2}$ are computed from the profile x_N supplied by the digital computer and from the two profiles being calculated. The derivative $\frac{\partial x}{\partial S}$ can be formed using the solution mass balance, to be integrated with respect to S for the two new profiles, $x_{N+\Delta N}(S)$ and $x_{N+2\ N}(S)$, for each of the two cells. The interfacial concentrations are calculated from the solution rate equation (Eqn 9-11) and the equilibrium relation (Eqn 9-13):-

$$x^* = x - \frac{1}{\rho} \cdot \frac{\partial \bar{y}}{\partial S}$$

$$y^* = \frac{Kx^*}{1 + (K - 1)x^*}$$

Integration of the three ordinary differential equations for the fickian particle rate expression (Eqns 8-3, with T replaced by S) give the particle concentrations. These provide the resin concentration gradient at the surface and the rate $\frac{\partial \bar{y}}{\partial S}$ from the particle mass balance (Eqn 9-10), required in the solution mass balance and the solution rate equation respectively. Details of the analog program are given in Appendix 9C.

The HIXM timing, interpolation and sampling methods were used without modification except that the micro-sweep time was made 2 msec, twenty-five times faster than for HIXM. The counter setting, NCNT (Figure 8C-1), was reduced to 20. With a portion of the SWEEP program (Appendix 8D) written in EAI-640 Assembler, the digital computer required 1.3 msec (out of the available 2.0 msec at each point in the profile) to respond to the analog computer request and to transfer and verify the information in both directions.

The finite-bed boundary condition introduced an iterative calculation for the concentration profile, $x_{N=0}(S)$, into the HIXL digital computer program. The boundary condition, Eqn (9-6a), became for complete exhaustion:-

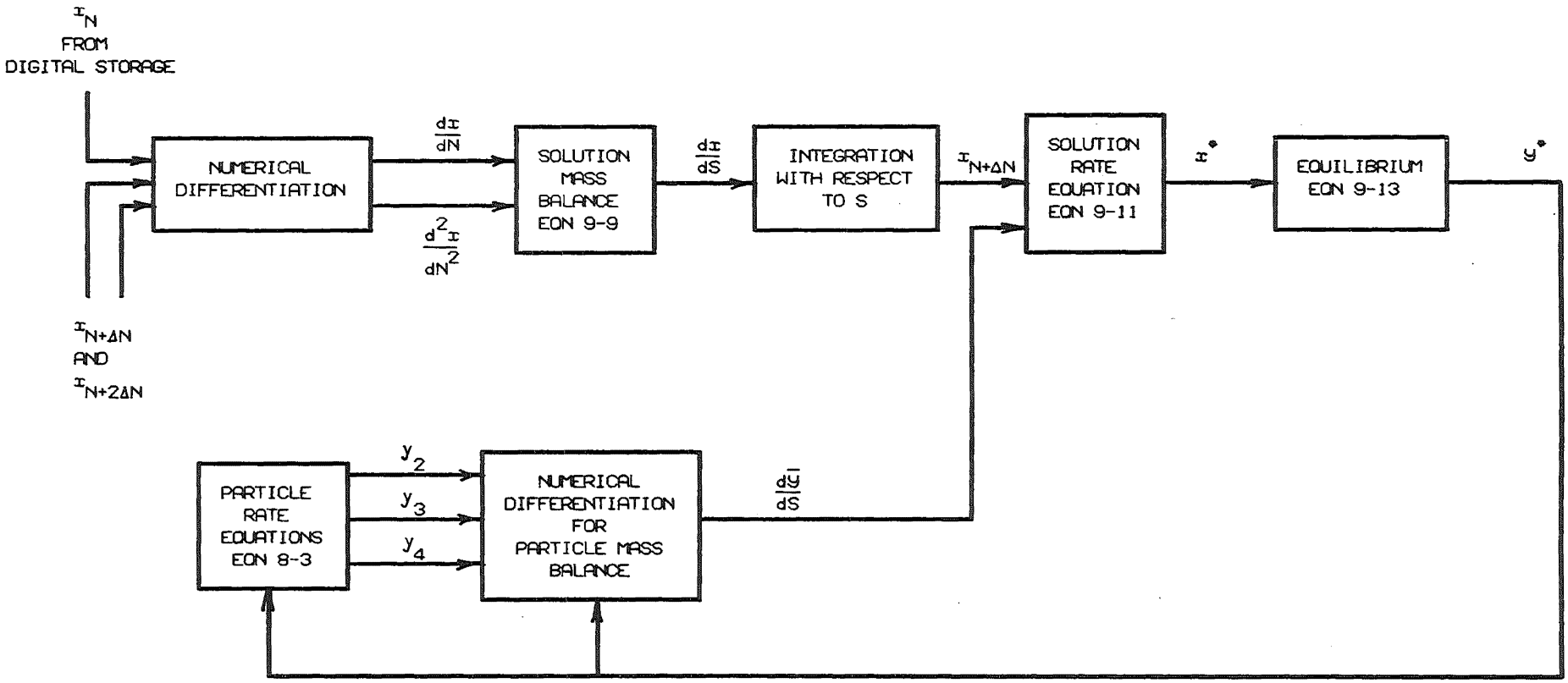


FIGURE 9-1. GENERAL ANALOG PROGRAMMING FOR HIXL.

$$x_{N=0} = 1.0 + \theta \left.\frac{\partial x}{\partial N}\right|_{N=0} \qquad (9\text{-}14)$$

The required derivative was calculated from the finite difference approximation (Eqn 8-2b)

$$\left.\frac{\partial x}{\partial N}\right|_{N=0} = -\frac{3x_{N=0} - 4x_{\Delta N} + x_{2\Delta N}}{2\Delta N} \qquad (9\text{-}15)$$

If some estimate of the function $x_{N=0}$ was made, a single analog computer sweep produced the profiles $x_{\Delta N}$ and $x_{2\Delta N}$. At the end of this sweep, the derivative could be calculated at each point on the profile from Eqn 9-15, and Eqn 9-14 could then be used to give better estimate of the $x_{N=0}$ profile. Iteration continued until all corresponding points on successive profiles agreed within 0.0020.

Graph 9-2 shows the approach of the method to convergence for a particular case ($K = 1.2$, $\xi = 0.0$, $\theta = 1.0$). While the iteration procedure is simple, it converged in fewer than ten iterations and was never unstable.

The profile iterations are shown on the plotted results from HIXL, e.g. Graph 9-15.

The infinite-bed boundary condition introduced a problem into HIXL that had not arisen in HIXM. The direction of integration in HIXL was not along a characteristic of Eqn 9-9. Consequently, the discontinuity of the unit step boundary condition could not dissipate into the solution along the characteristics (Ames, 1969) and problems occurred in the evaluation of the derivatives $\frac{\partial x}{\partial N}$ and $\frac{\partial^2 x}{\partial N^2}$.

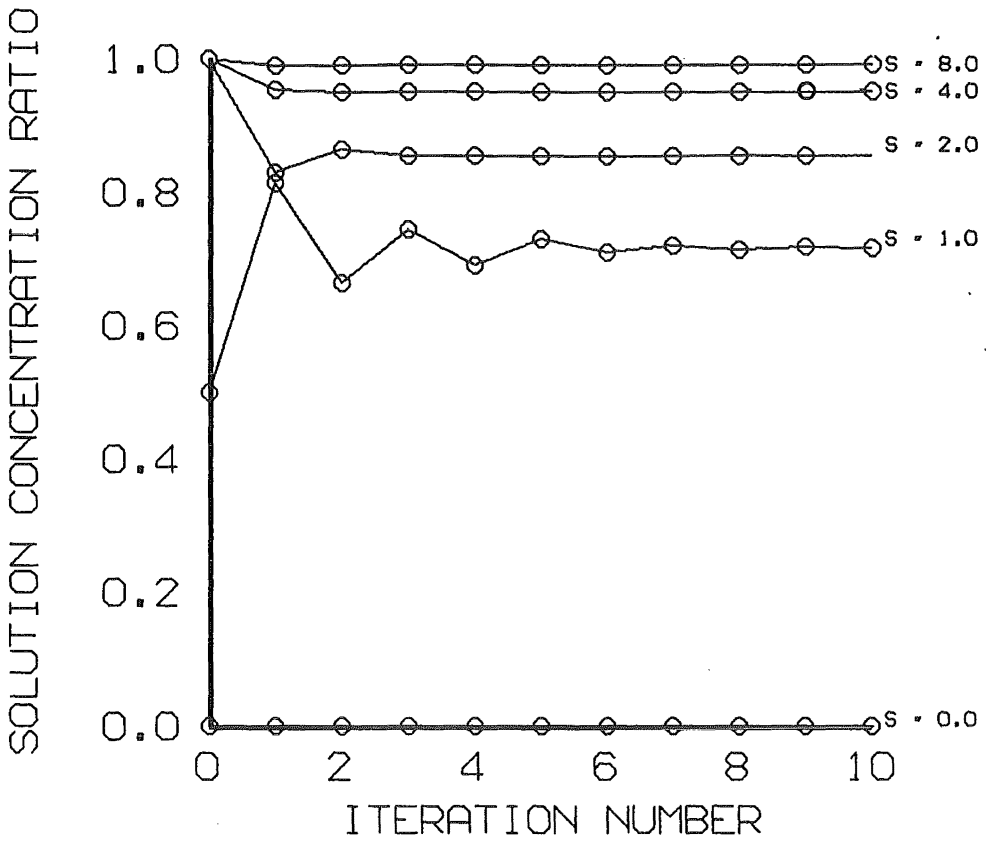
At T = 0, for the first sweep,

$$x_{N=0} = 1.0$$
$$x_{\Delta N} = 0.0$$
$$x_{2\Delta N} = 0.0$$

and, from Eqns 9C-3, 9C-4, the derivatives are:-

$$\left.\frac{\partial x}{\partial N}\right|_{\Delta N} = -\tfrac{1}{2} \qquad \left.\frac{\partial x}{\partial N}\right|_{2\Delta N} = \tfrac{1}{2}$$

for $\Delta N = 1.0$ and no axial dispersion. Since the rate, $\frac{d\bar{y}}{dS}$, is zero



GRAPH 9-2. CONVERGENCE OF FINITE BED BOUNDARY CONDITION.

$K = 1.2$ $\xi = 0.0$ $\theta = 1.0$

the gradients are (Eqn 9C-1)

$$\left.\frac{\partial x}{\partial S}\right|_{\Delta N} = - BD_R\left(\frac{\partial x}{\partial N}\right) = \frac{BD_R}{2}$$

$$\left.\frac{\partial x}{\partial S}\right|_{2\Delta N} = - BD_R(+\tfrac{1}{2}) = - \frac{BD_R}{2}$$

Upon integration, the breakthrough curve $x_{2\Delta N}$ will initially become negative, and remain so for a short period.

The problem was resolved by replacing the step function by the approximate form shown in Figure 9-2. Since the step-sizes ΔS was small, the effect of this approximation should be negligible.

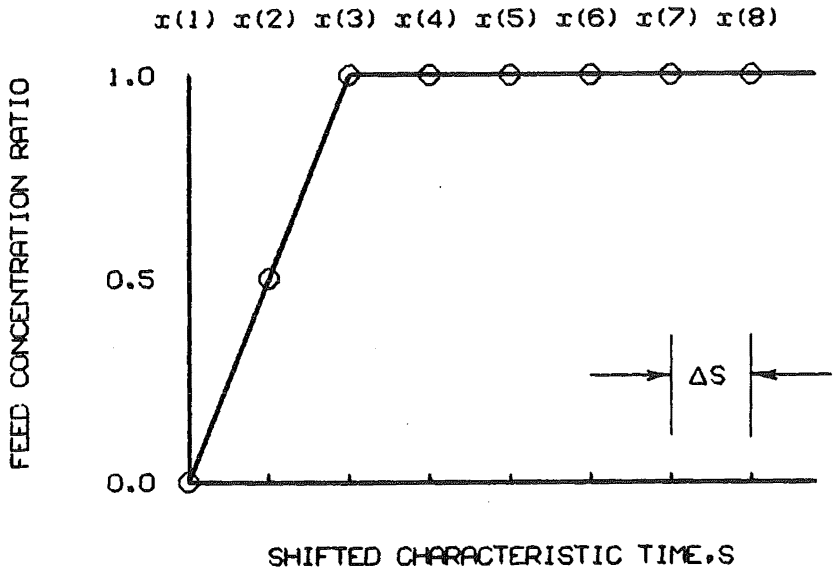


FIGURE 9-2. INFINITE-BED BOUNDARY CONDITION FOR HIXL TO APPROXIMATE FEED CONCENTRATION HISTORY.

9-6 ACCURACY WITH HIXL

Inaccuracy in the analog computer prevented the HIXL simulation from attaining correct steady-state values. Graph 9-3 shows a particularly bad example, with the final steady-state value falling to 99.3% of the input at each sweep. After 10 sweeps the breakthrough curve has risen to only 0.93. The robustness and self-regulation of HIXM is absent in HIXL.

This graph is also of interest in that it shows the serious effect of the loss of a single high-order bit between the two computers.

The error analysis in Appendix 9D for the analog portion of HIXL shows that for accuracy:-

(a) the step-size ΔN should be kept small

(b) the number of sweeps should be minimised, in conflict with (a)

(c) the potentiometers set to C3 and C4 in Figure 9D-1 must be carefully set, especially in the first analog cell.

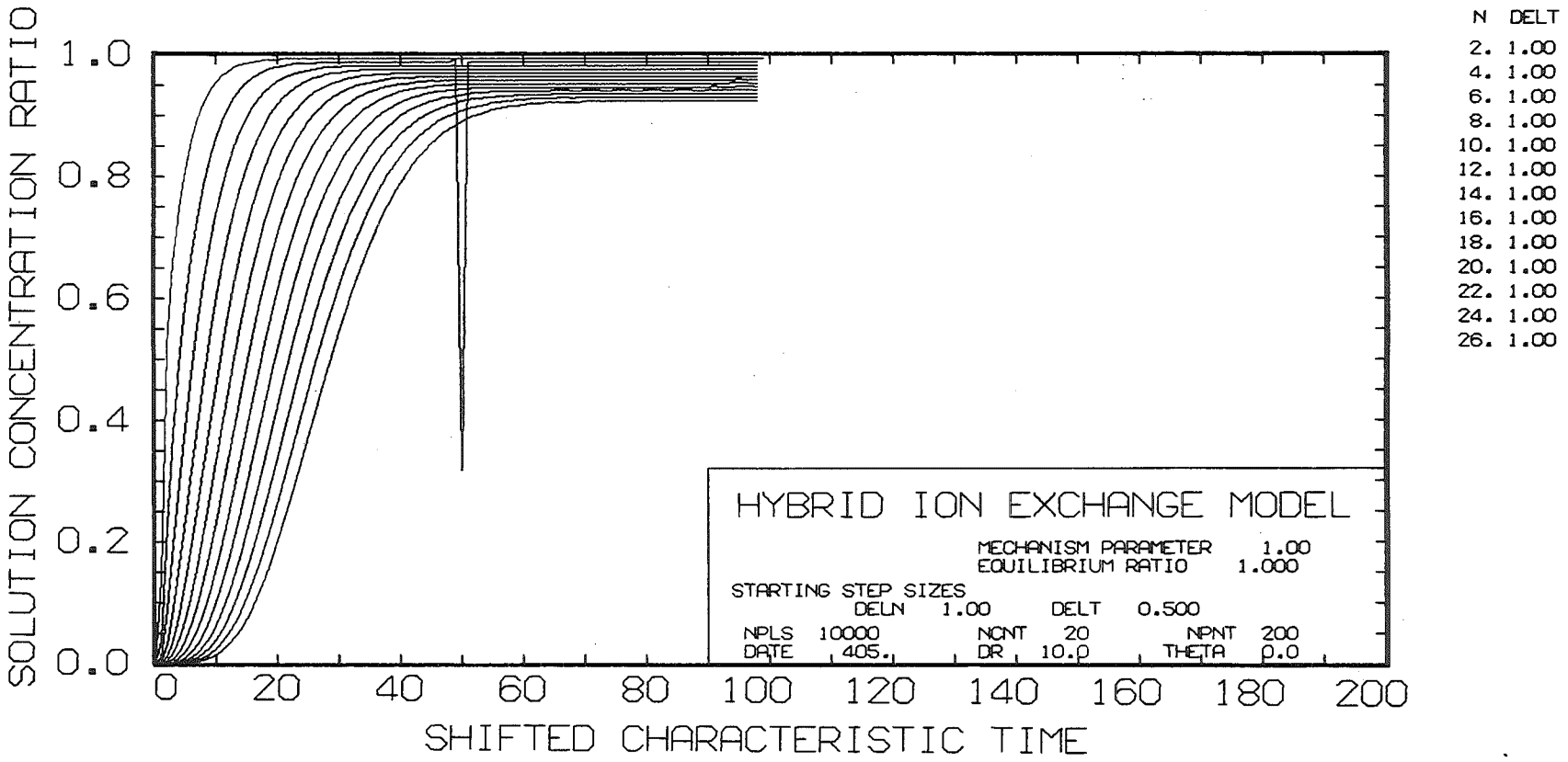
9-7 STEP-SIZE SELECTION AND VERIFICATION

Repeated runs with decreasing step-sizes established appropriate step-sizes before any results were plotted. In general, the starting values:-

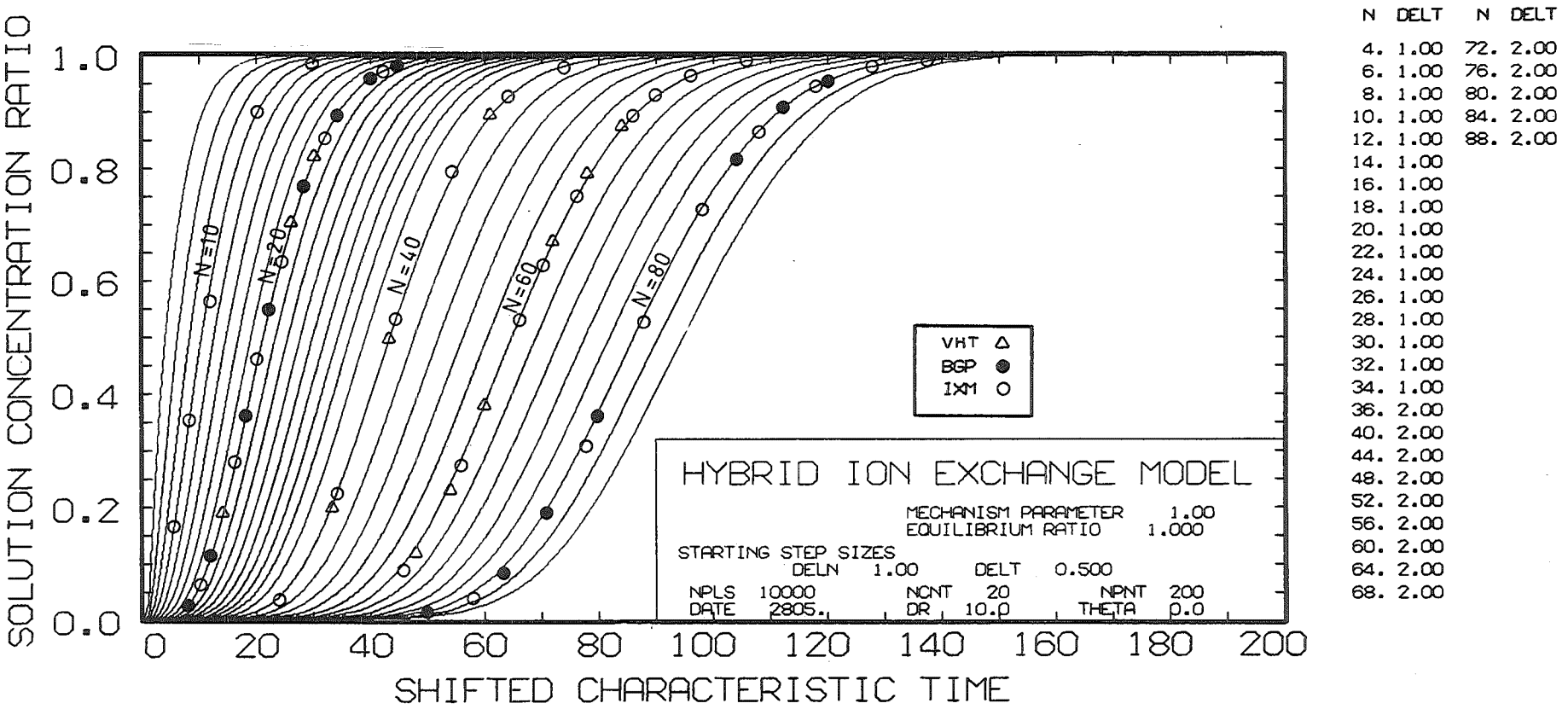
$$\Delta N = 1.0 \qquad \Delta T = 0.5$$

were satisfactory, with each doubled once. Fewer step-size changes required less time to be spent setting potentiometers. This and the twenty-five fold increase in analog speed meant that HIXL was much faster than HIXM.

For linear equilibrium with no axial dispersion, the results from HIXL should be equivalent to Rosen's or to those of the more general but equivalent BGP program. Graphs 9-4 to 9-6 compare these, and also results from the digital computer model, IXM, for values of the mechanism parameter of 1.0, 0.5 and 2.0 respectively. The boundary condition used was for the infinite bed. In general, agreement is good, the maximum error being 0.01 in the solution concentration occurring at higher values of N. This verifies the general nature

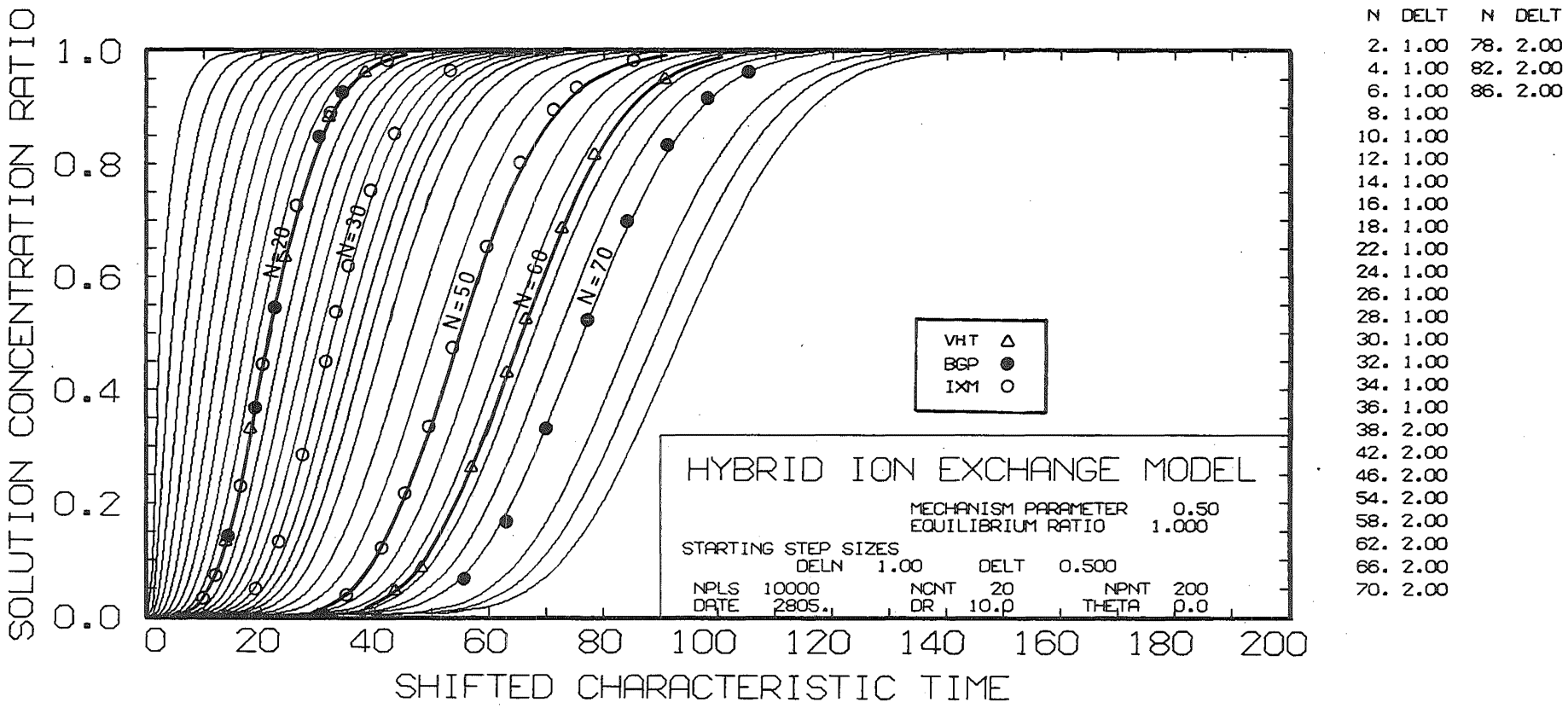


GRAPH 9-3. COMPUTING INACCURACY IN HIXL.



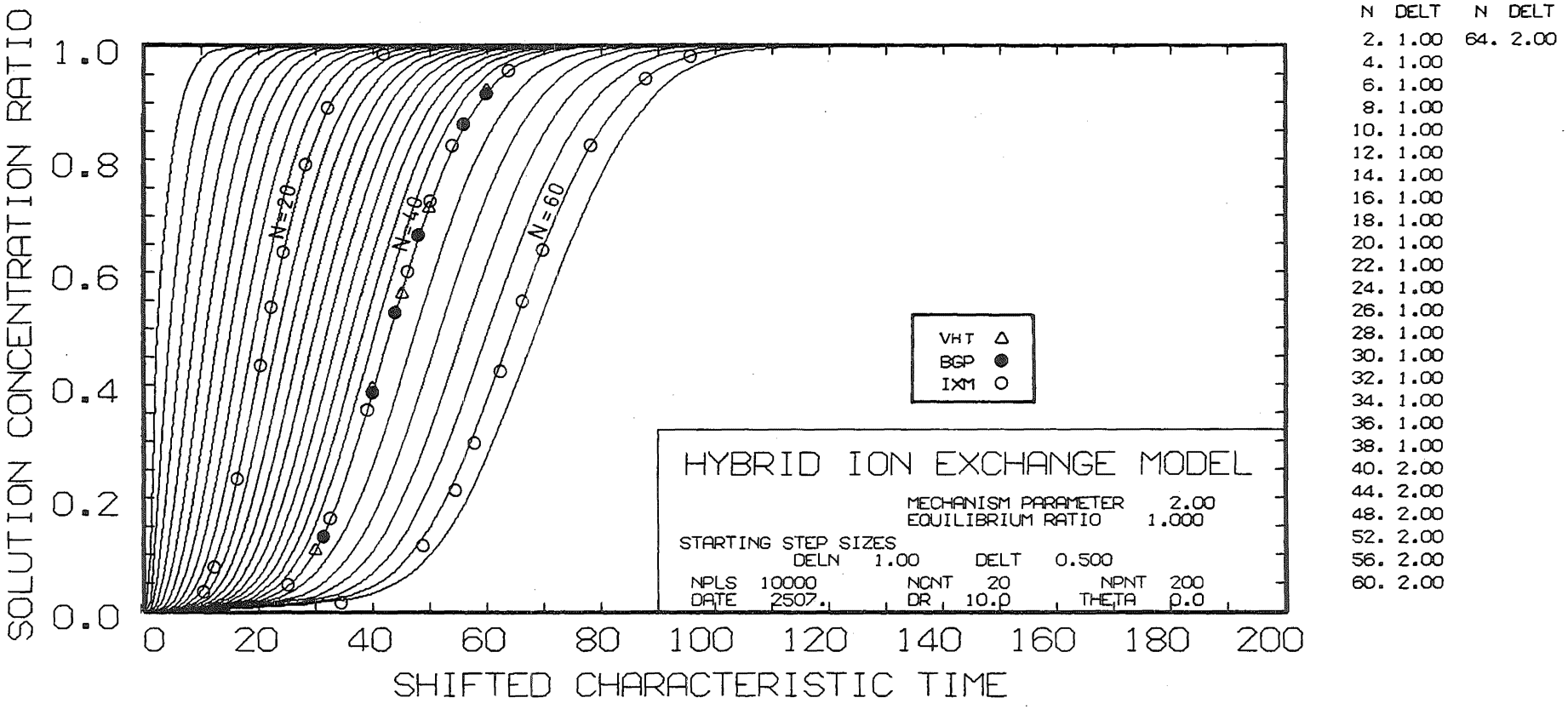
N	DELT	N	DELT
4.	1.00	72.	2.00
6.	1.00	76.	2.00
8.	1.00	80.	2.00
10.	1.00	84.	2.00
12.	1.00	88.	2.00
14.	1.00		
16.	1.00		
18.	1.00		
20.	1.00		
22.	1.00		
24.	1.00		
26.	1.00		
28.	1.00		
30.	1.00		
32.	1.00		
34.	1.00		
36.	2.00		
40.	2.00		
44.	2.00		
48.	2.00		
52.	2.00		
56.	2.00		
60.	2.00		
64.	2.00		
68.	2.00		

GRAPH 9-4. VERIFICATION OF HIXL AGAINST IXM AND BGP FOR LINEAR EQUILIBRIUM AND NO AXIAL DISPERSION. VHT POINTS ARE INCLUDED FOR COMPARISON.



N	DELT	N	DELT
2.	1.00	78.	2.00
4.	1.00	82.	2.00
6.	1.00	86.	2.00
8.	1.00		
10.	1.00		
12.	1.00		
14.	1.00		
16.	1.00		
18.	1.00		
22.	1.00		
24.	1.00		
26.	1.00		
28.	1.00		
30.	1.00		
32.	1.00		
34.	1.00		
36.	1.00		
38.	2.00		
42.	2.00		
46.	2.00		
54.	2.00		
58.	2.00		
62.	2.00		
66.	2.00		
70.	2.00		

GRAPH 9-5. VERIFICATION OF HIXL AGAINST IXM AND BGP FOR LINEAR EQUILIBRIUM AND NO AXIAL DISPERSION. VHT POINTS ARE INCLUDED FOR COMPARISON.



GRAPH 9-6. VERIFICATION OF HIXL AGAINST IXM AND BGP FOR LINEAR EQUILIBRIUM AND NO AXIAL DISPERSION. VHT POINTS ARE INCLUDED FOR COMPARISON.

of the method, and its predictions at linear equilibrium.

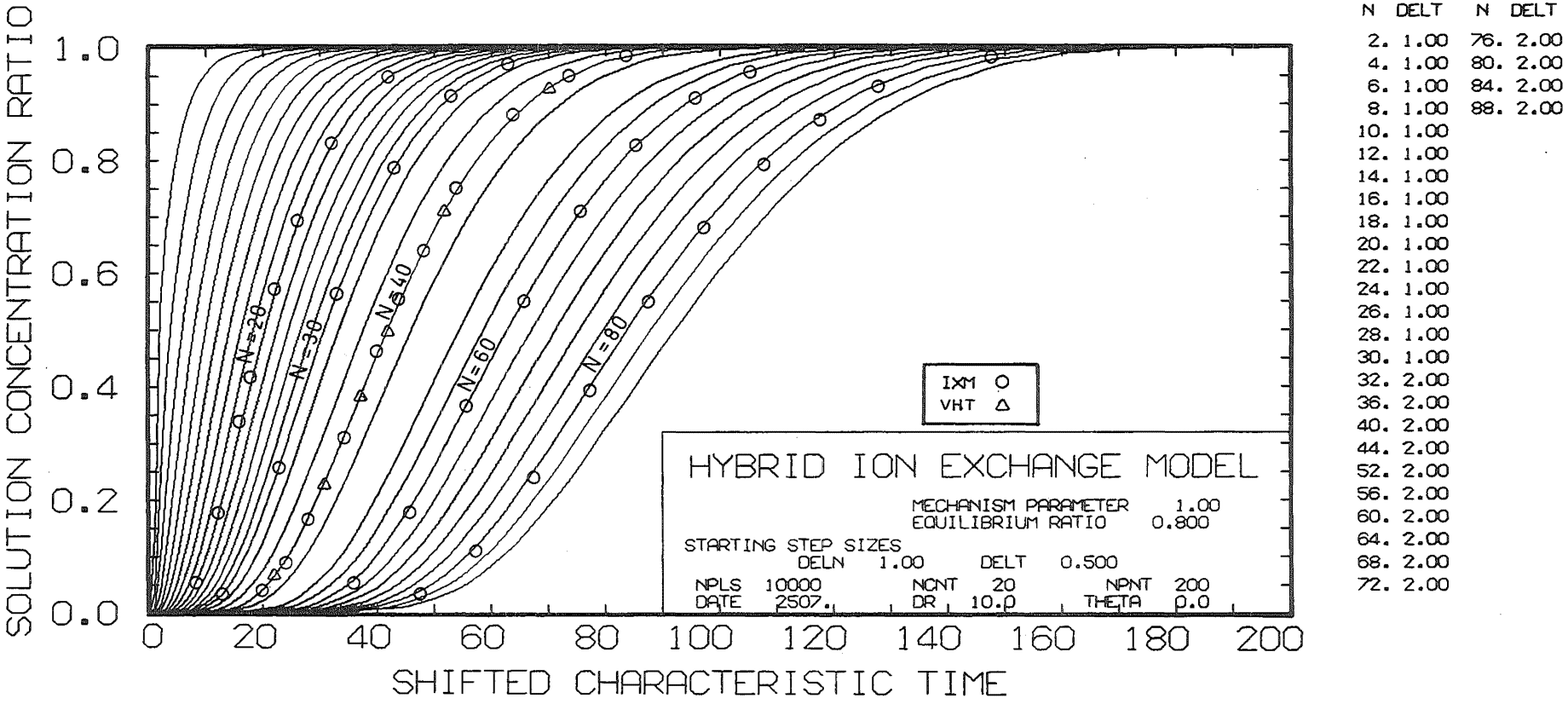
For non-linear equilibrium, graphs 9-7 and 9-8 compare HIXL with IXM and HIXM at separation factors of 0.8 and 1.2. Again, the agreement is sufficiently good (especially at N below about 60) suggesting that HIXL correctly incorporates equilibrium effects. At N = 100, there is a difference of about one unit in the characteristic time between HIXM and HIXL.

The correctness of the small section in the analog circuit which generates the axial dispersion effects was verified against the BGP program (Graph 9-9), but only for linear equilibrium and for the infinite-bed boundary condition. However, the graph does include both boundary conditions up to 20 transfer units; thereafter the curves were too close to be separated.

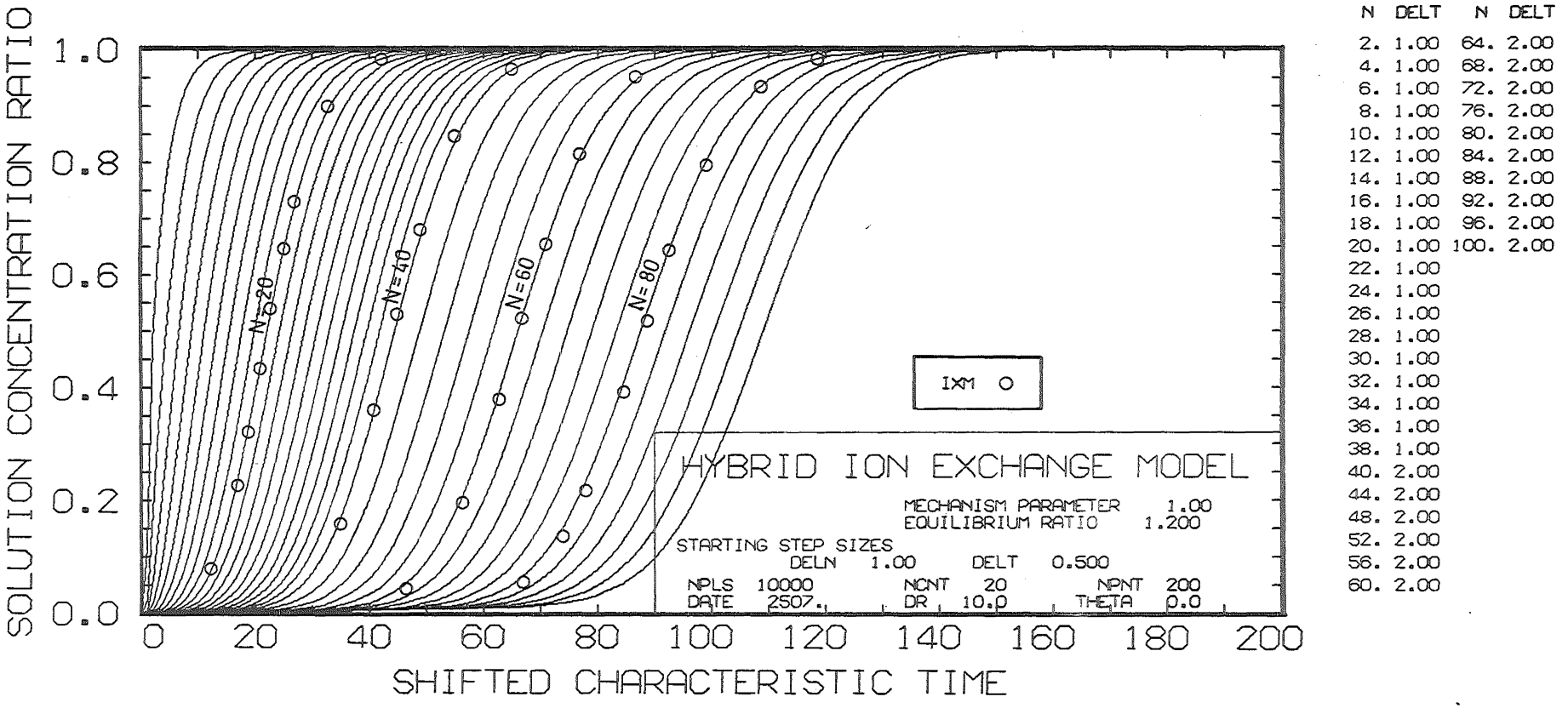
This verifies the iterative calculation for the first profile of the finite-bed boundary condition. Further, Table 9-3 lists an assumed profile (which is in fact the $x_{N=0}$ profile used for the infinite column condition and is the first estimate of the finite bed profile) and the computed breakthrough curves from the two cells of the analog computer, at 1 and 2 transfer units. From these values, and Eqns 9-14 and 9-15, the new profile $x_{N=0}$ has been calculated by hand and compared with the digital computer values.

Whilst there is no solution available to test simulatneously the full features of HIXL, all the parts of the computational model have been tested and used to produce a range of results which have been compared with available solutions. Agreement has been within the accuracy of the equipment, the structure of the model and the method of solution, and the hybrid computer model can be readily accepted as an adequate simulation of the fixed-bed ion exchange process.

For less than 40 transfer units, the accuracy has been 1% or better, but errors of up to 2% have occurred at 80 transfer units.

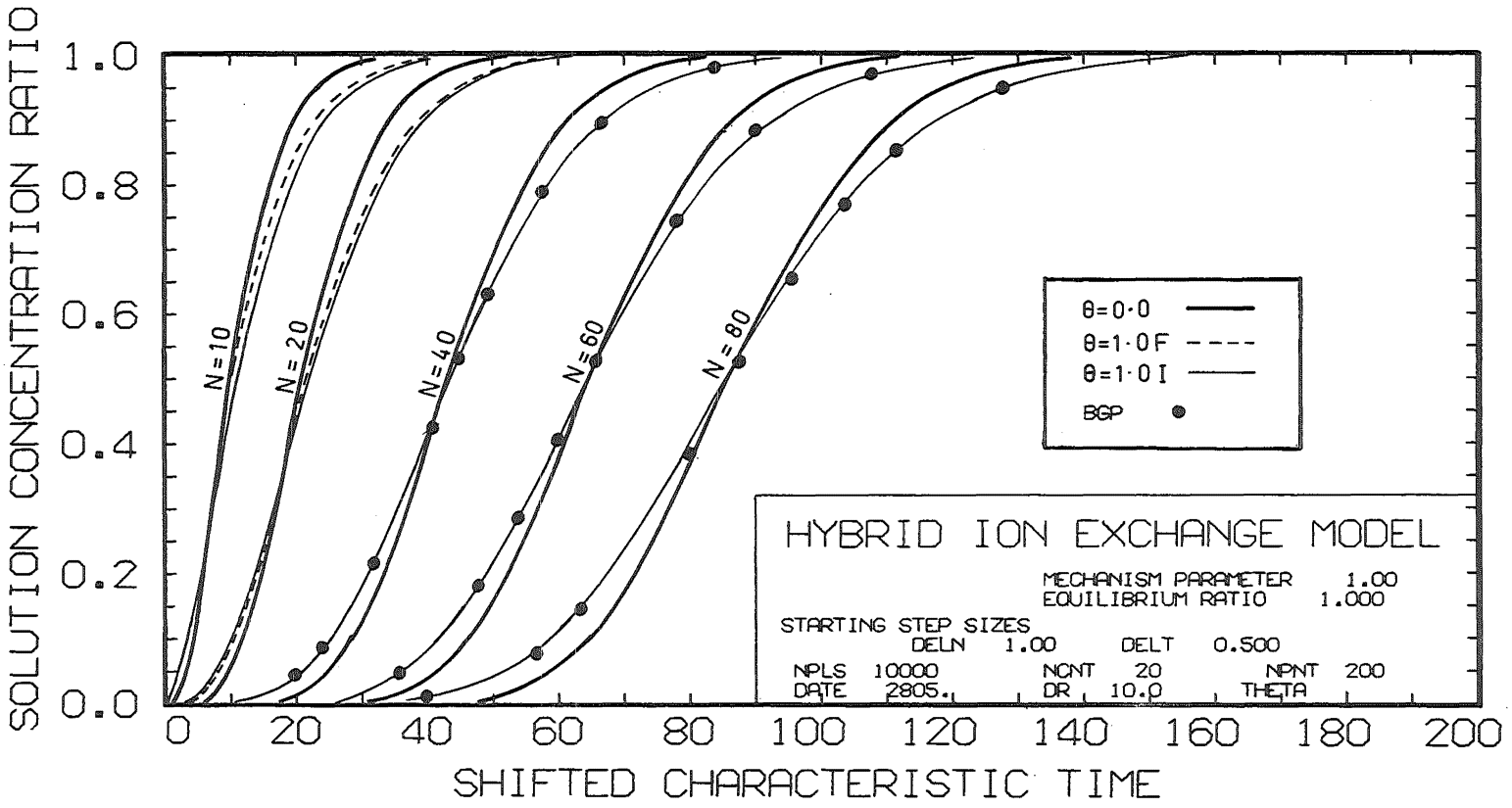


GRAPH 9-7. VERIFICATION OF HIXL AGAINST IXM FOR UNFAVOURABLE EQUILIBRIUM AND NO AXIAL DISPERSION. VHT POINTS ARE INCLUDED FOR COMPARISON.

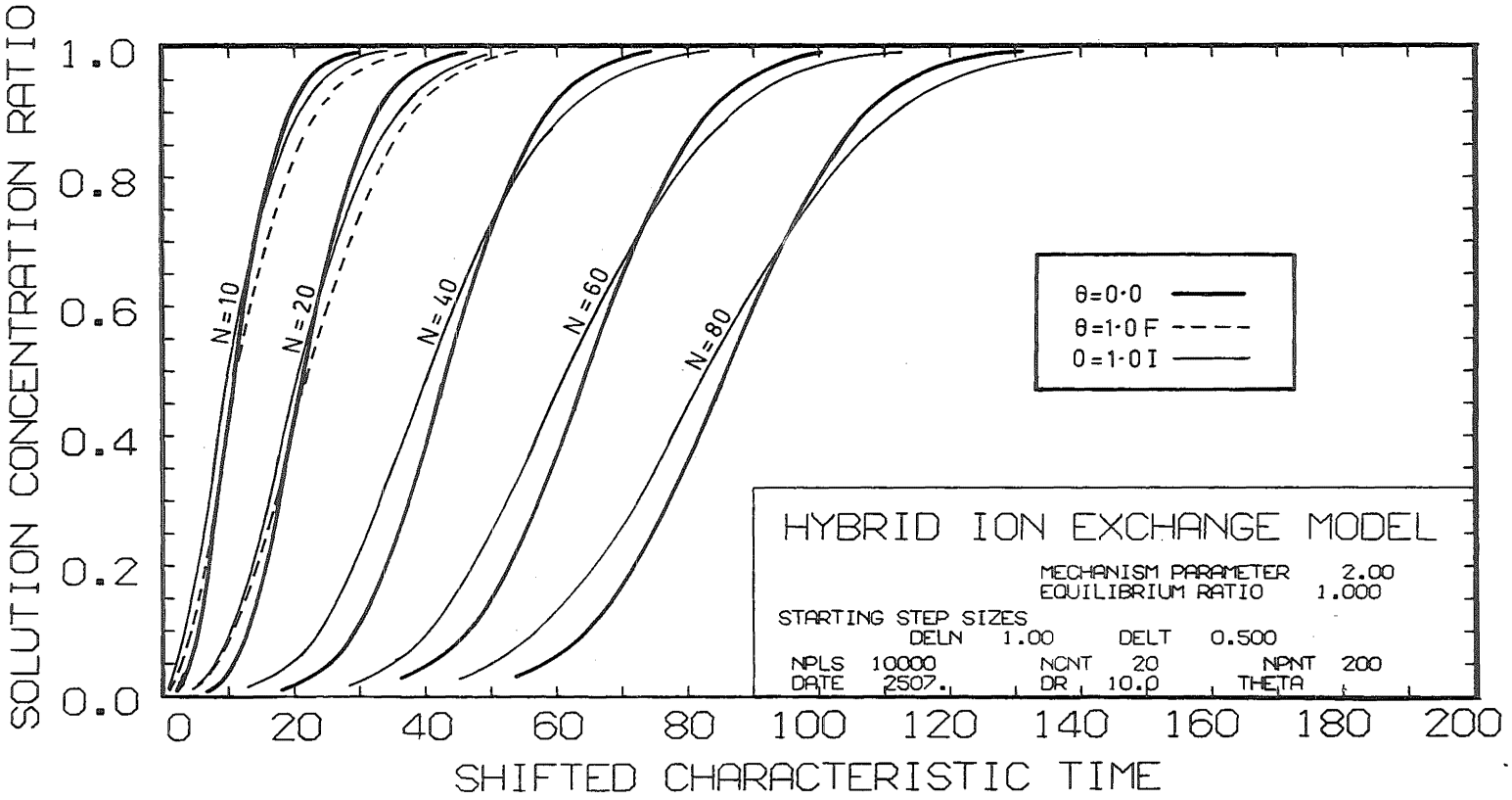


N	DELT	N	DELT
2.	1.00	64.	2.00
4.	1.00	68.	2.00
6.	1.00	72.	2.00
8.	1.00	76.	2.00
10.	1.00	80.	2.00
12.	1.00	84.	2.00
14.	1.00	88.	2.00
16.	1.00	92.	2.00
18.	1.00	96.	2.00
20.	1.00	100.	2.00
22.	1.00		
24.	1.00		
26.	1.00		
28.	1.00		
30.	1.00		
32.	1.00		
34.	1.00		
36.	1.00		
38.	1.00		
40.	2.00		
44.	2.00		
48.	2.00		
52.	2.00		
56.	2.00		
60.	2.00		

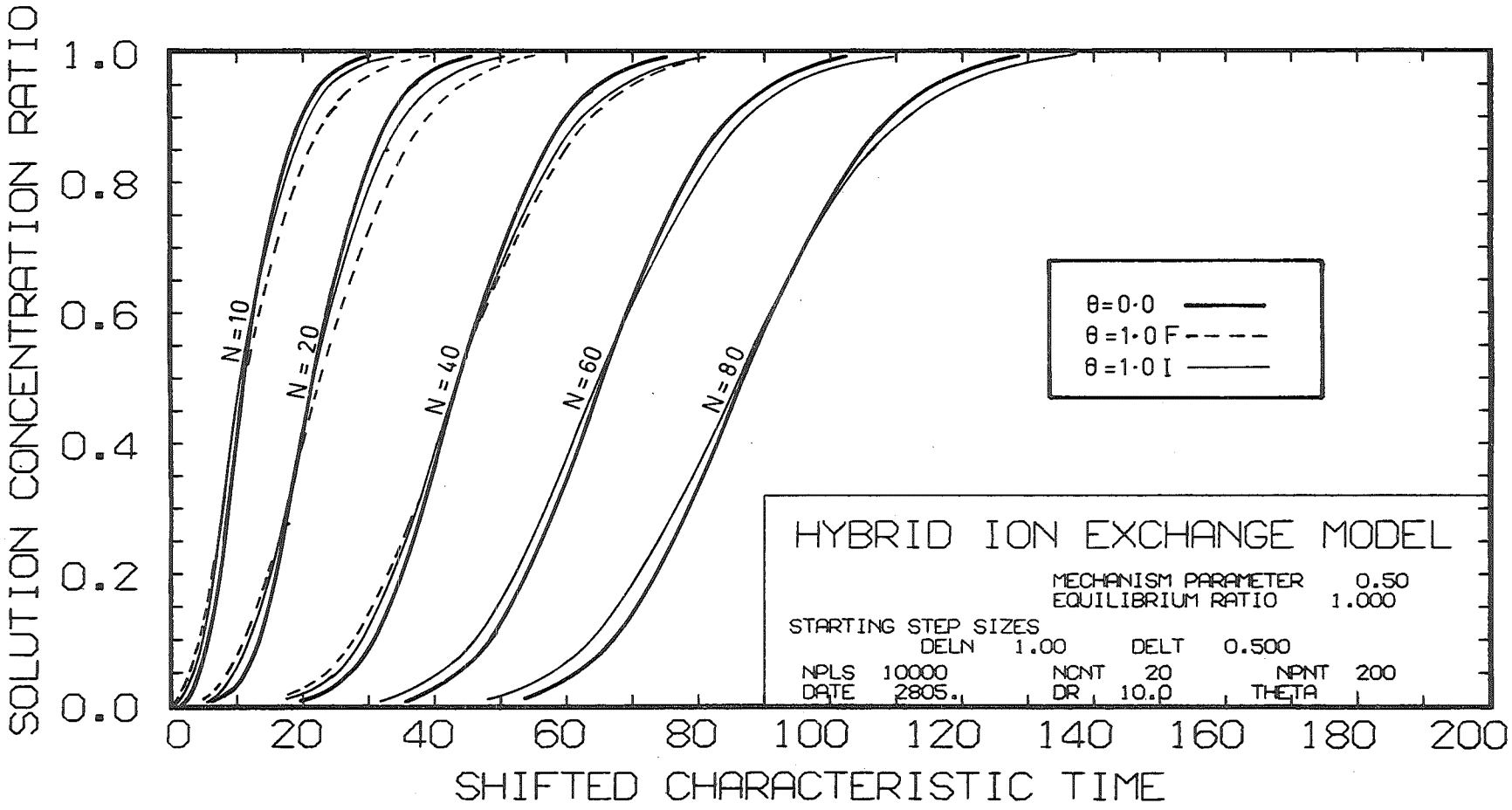
GRAPH 9-8. VERIFICATION OF HIXL AGAINST IXM FOR FAVOURABLE EQUILIBRIUM AND NO AXIAL DISPERSION.



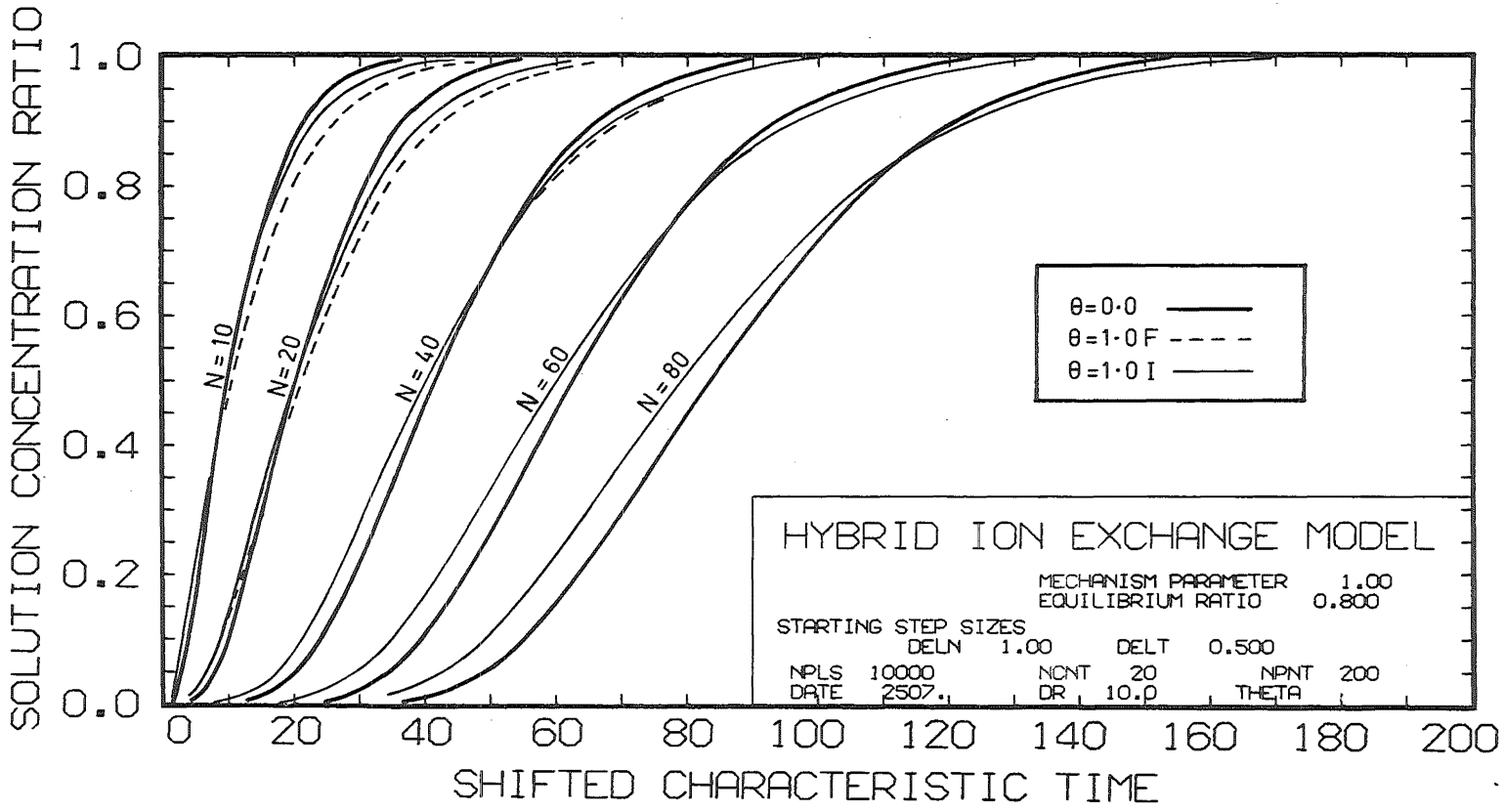
GRAPH 9-9. VERIFICATION OF HIXL AGAINST BGP FOR LINEAR EQUILIBRIUM AND AXIAL DISPERSION.



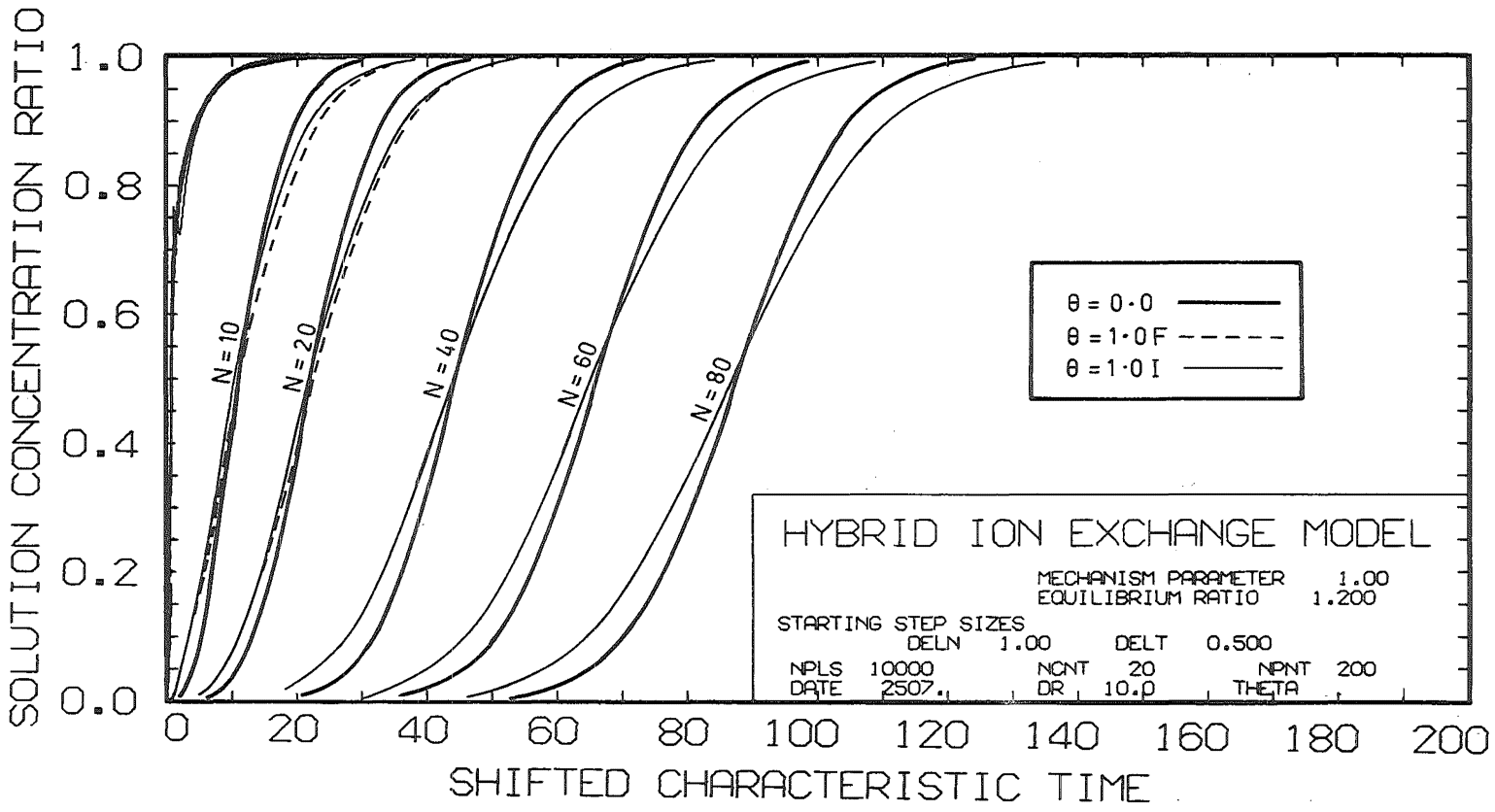
GRAPH 9-10. HIXL RESULTS.



GRAPH 9-11. HIXL RESULTS.



GRAPH 9-12. HIXL RESULTS.



GRAPH 9-13. HIXL RESULTS.

Assumed Initial Profile	Computer Profiles		Iterated Initial Profile	Hand Verification
$x_{N=0}$	$x_{\Delta N}$	$x_{2\Delta N}$	$x'_{N=0}$	$x'_{N=0}$
0	.0257	.0120	0.0	0.0
.5	.2882	.2039	.8622	.8622
.99988	.6983	.5271	.8166	.8166
.99988	.8067	.6806	.8867	.8866
.99988	.8612	.7683	.9192	.9192
.99988	.8978	.8315	.9400	.9400
.99988	.9240	.8796	.9542	.9542
.99988	.9434	.9165	.9643	.9643
.99988	.9581	.9450	.9719	.9720

$K = 1.0$ $\xi = 1.0$ $\theta = 0.5$

$\Delta N = 1.0$ $\Delta T = 1.0$

TABLE 9-3. Verification of the iteration for the finite-bed boundary condition.

9-8 COMPUTED RESULTS

With the introduction of axial dispersion into the model of the fixed-bed ion exchange process, the number of parameters needed to identify the system has grown to 5 (i.e. K, ξ, N, θ, D_R). Too many results would have to be calculated to permit the production of generalised breakthrough curves (analogous to those produced for IXLR in Appendix 5E). Sufficient results have been generated to indicate the effect of the axial dispersion parameters. These are summarised in 5 plots

Graph	K	ξ
9-9	1.0	1.0
9-10	1.0	2.0
9-11	1.0	0.5
9-12	0.8	1.0
9-13	1.2	1.0

each of which includes dispersion parameter values of 0.0 and 1.0 for distribution ratios of 10.0 and 100.0, for up to 80 transfer units.

9-8-1 The Effect of Axial Dispersion

As the axial dispersion parameter increases the width of the breakthrough curve increases, as is well-known and to be expected. However, Graphs 9-9 to 9-13 show that the shape of the curves has not changed, merely the slope. One could not say, from an isolated breakthrough curve whether spreading had been caused by axial dispersion or any other mechanism.

9-8-2 The Finite Bed Boundary Conditions

Each group shows that for more than 20 transfer units, the difference between the two boundary conditions applying at the top of column is negligible. While this has little computational significance for the hybrid computer solution (and probably not for a digital computer solution either), this conclusion is important in any attempt to provide further analytical expressions, for which the infinite bed condition is more tractable.

9-8-3 The Distribution Ratio

In the absence of axial dispersion, breakthrough curves can be

plotted against the characteristic time and are functions of K, ξ and N. Altering the distribution ratio, D_R ($= \frac{Q}{\varepsilon C_o}$) while keeping the number of transfer units constant will have no effect. If, however, the curves are plotted against the shifted characteristic time, S, which is related to the characteristic time by Eqn 9-14:-

$$S = T + \frac{N}{D_R}$$

then changing the distribution ratio from D_{R1} to D_{R2} will displace the breakthrough curve $N(\frac{1}{D_{R1}} - \frac{1}{D_{R2}})$ units in S.

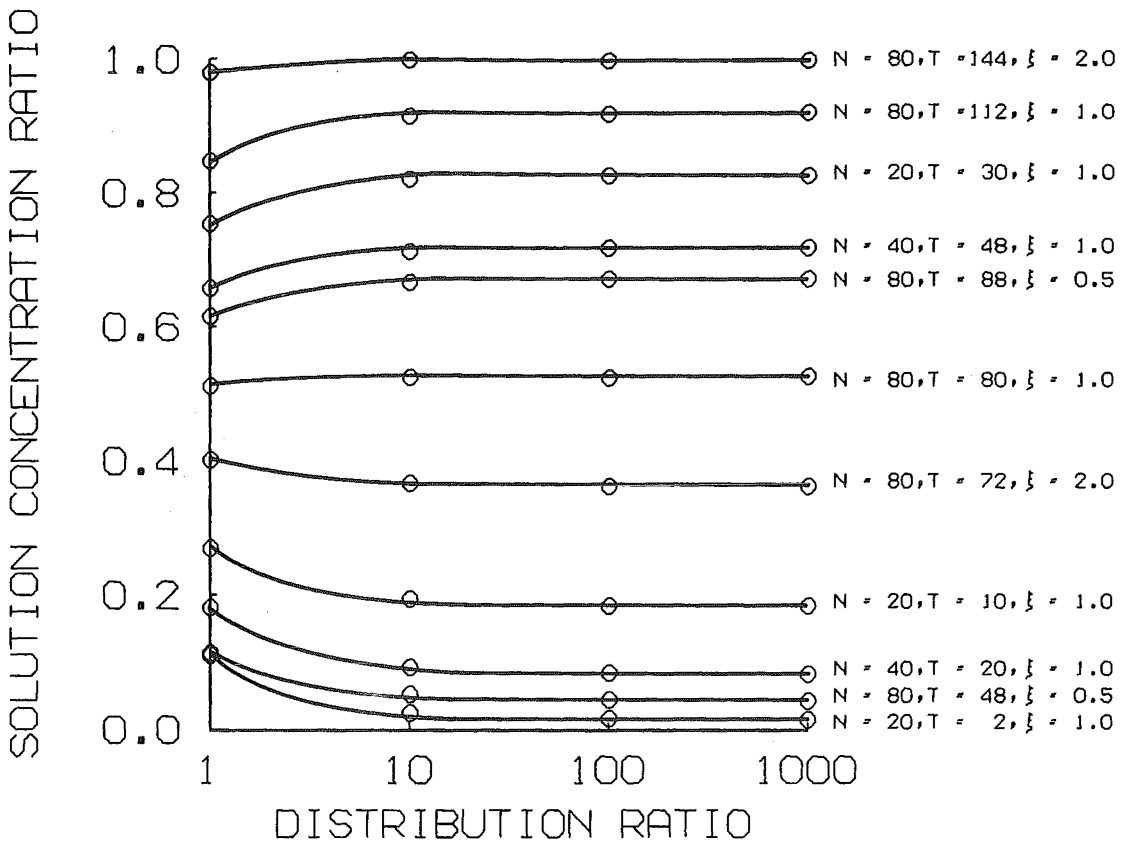
Solution concentration ratios have been calculated from the BGP program for linear equilibrium and significant dispersion ($\theta = 1.0$) with the distribution ratio increasing from 1.0 to 1000.0 at the indicated values of ξ, N, T. Practical ion exchange values of the distribution ratio are greater than 10 (unless dealing with either a very concentrated solution, probably uneconomic for ion exchange separation, or a resin with low capacity). For the values of interest, Graph 9-14 shows that the distribution ratio is not significant, at least for linear equilibrium.

Further linear equilibrium results for HIXL are plotted against the shifted characteristic time in Graph 9-15 for $D_R = 100$ and $D_R = 10$ (superimposed). The breakthrough curves at 10,20,40,60,80 transfer units are the same shape for the two distribution ratios and are correctly displaced by 0.9, 1.8, 3.6, 5.4 and 7.2 units in S.

Graphs 9-16 and 9-17 give similar results for non-linear equilibrium. The shape of the computed breakthrough curves is independent of the distribution ratio, extending the conclusion above to non-linear equilibrium.

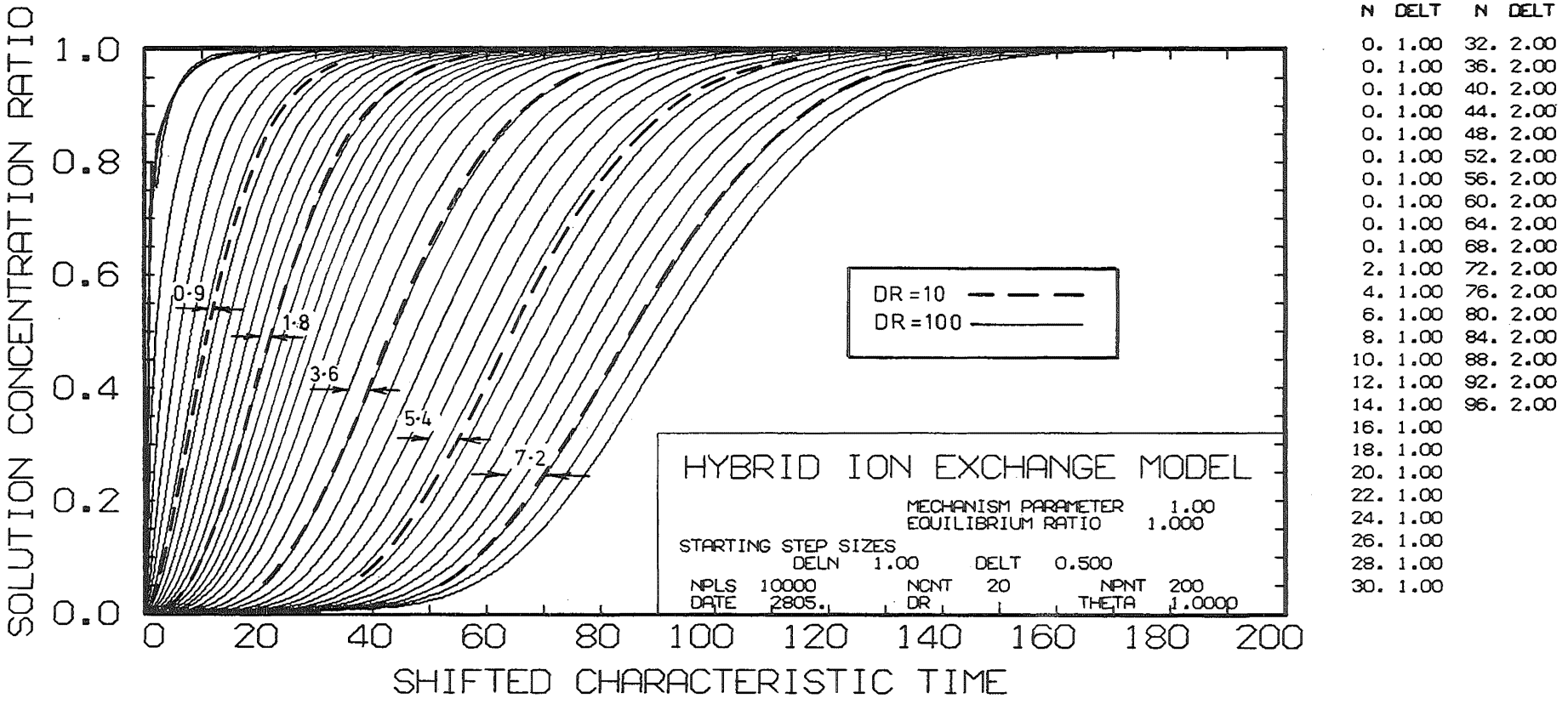
9-9 THE APPROXIMATE EXPRESSION OF AXIAL DISPERSION EFFECTS

The reaction-kinetic method of predicting ion exchange column behaviour, developed by Vermeulen, Hiester and Thomas (Section 3-4) will be shown (Section 10- 2) to provide a reasonable expression of breakthrough curves. A number of the graphs in this chapter include points calculated by the VHT method which are in agreement with other computed results.



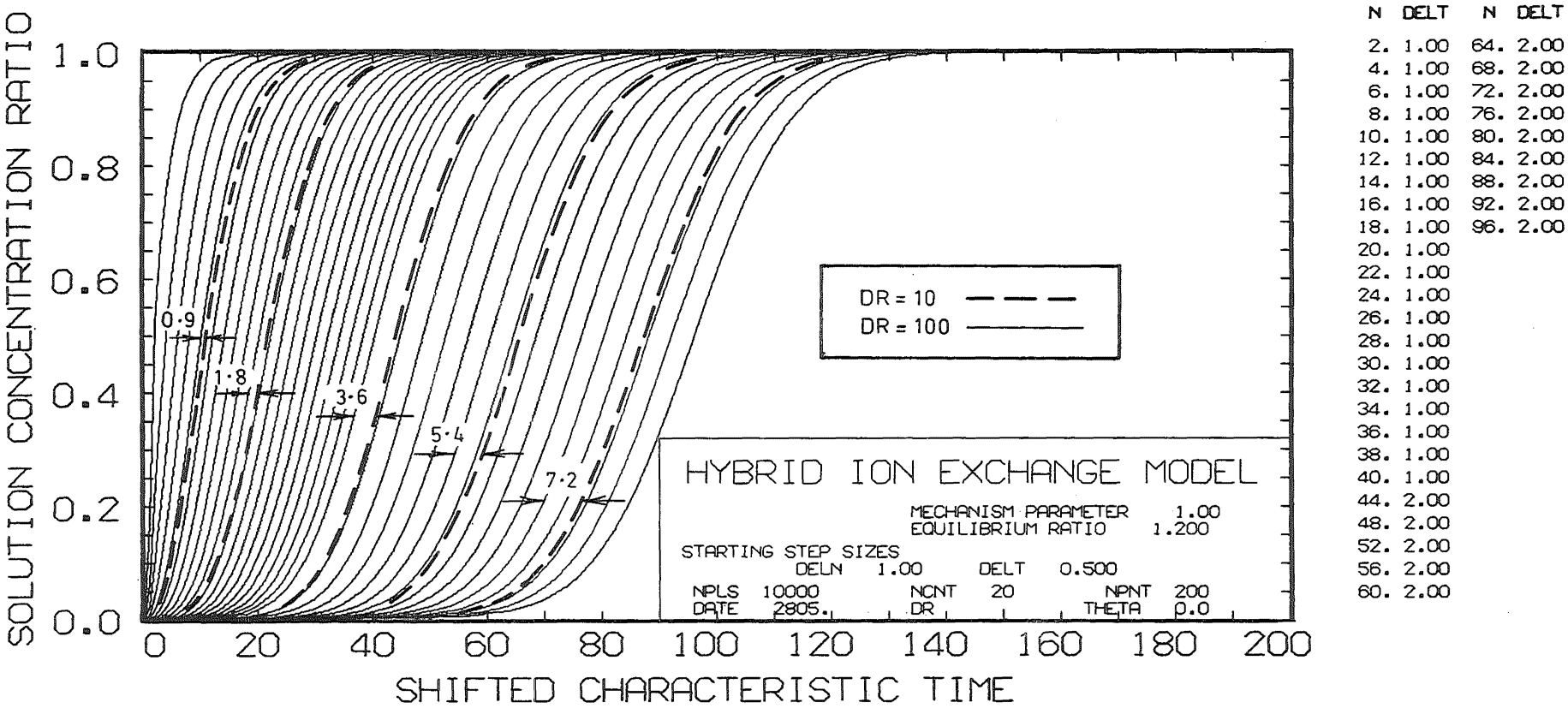
$K = 1.0 \quad \theta = 1.0$

GRAPH 9-14. THE EFFECT OF DISTRIBUTION RATIO ON BREAKTHROUGH CURVE VALUES.



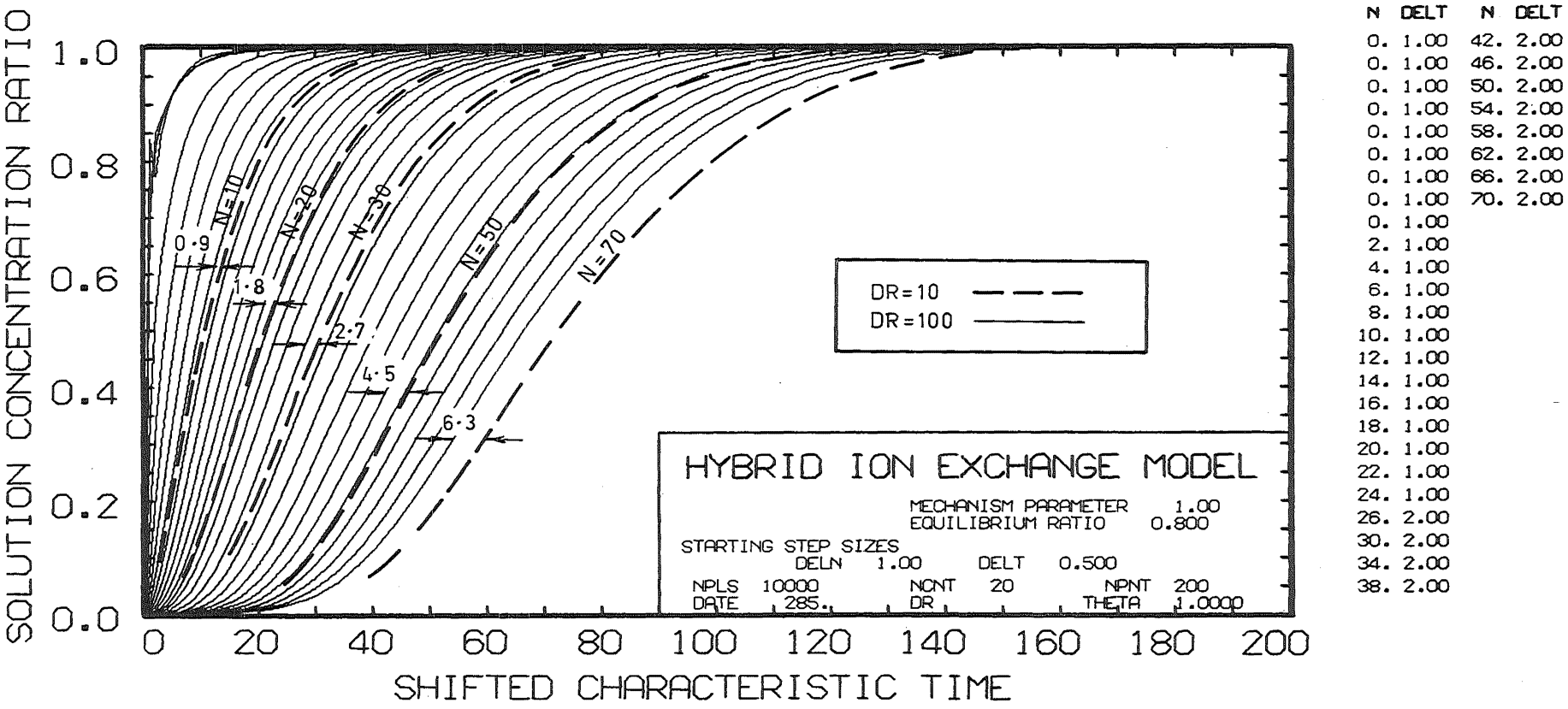
N	DELT	N	DELT
0.	1.00	32.	2.00
0.	1.00	36.	2.00
0.	1.00	40.	2.00
0.	1.00	44.	2.00
0.	1.00	48.	2.00
0.	1.00	52.	2.00
0.	1.00	56.	2.00
0.	1.00	60.	2.00
0.	1.00	64.	2.00
0.	1.00	68.	2.00
2.	1.00	72.	2.00
4.	1.00	76.	2.00
6.	1.00	80.	2.00
8.	1.00	84.	2.00
10.	1.00	88.	2.00
12.	1.00	92.	2.00
14.	1.00	96.	2.00
16.	1.00		
18.	1.00		
20.	1.00		
22.	1.00		
24.	1.00		
26.	1.00		
28.	1.00		
30.	1.00		

GRAPH 9-15. THE EFFECT OF THE DISTRIBUTION RATIO ON BREAKTHROUGH CURVE SHAPE FOR LINEAR EQUILIBRIUM.



N	DELT	N	DELT
2.	1.00	64.	2.00
4.	1.00	68.	2.00
6.	1.00	72.	2.00
8.	1.00	76.	2.00
10.	1.00	80.	2.00
12.	1.00	84.	2.00
14.	1.00	88.	2.00
16.	1.00	92.	2.00
18.	1.00	96.	2.00
20.	1.00		
22.	1.00		
24.	1.00		
26.	1.00		
28.	1.00		
30.	1.00		
32.	1.00		
34.	1.00		
36.	1.00		
38.	1.00		
40.	1.00		
44.	2.00		
48.	2.00		
52.	2.00		
56.	2.00		
60.	2.00		

GRAPH 9-16. THE EFFECT OF THE DISTRIBUTION RATIO ON BREAKTHROUGH CURVE SHAPE FOR FAVOURABLE EQUILIBRIUM.



N	DELT	N	DELT
0.	1.00	42.	2.00
0.	1.00	46.	2.00
0.	1.00	50.	2.00
0.	1.00	54.	2.00
0.	1.00	58.	2.00
0.	1.00	62.	2.00
0.	1.00	66.	2.00
0.	1.00	70.	2.00
0.	1.00		
2.	1.00		
4.	1.00		
6.	1.00		
8.	1.00		
10.	1.00		
12.	1.00		
14.	1.00		
16.	1.00		
18.	1.00		
20.	1.00		
22.	1.00		
24.	1.00		
26.	2.00		
30.	2.00		
34.	2.00		
38.	2.00		

GRAPH 9-17. THE EFFECT OF THE DISTRIBUTION RATIO ON BREAKTHROUGH CURVE SHAPE FOR UNFAVOURABLE EQUILIBRIUM.

The VHT method uses a two parameter model, the separation factor, K, and the number of reaction transfer units, N_R. A relation has been provided between the number of film and particle transfer units and the reaction transfer units (Eqn 3-24);

$$\frac{b}{N_R} = \frac{1}{N_p} + \frac{1}{N_f}$$

where b is a correction factor for non-linear equilibrium. To modify the VHT method to include axial dispersion effects, an equation like Eqn 3-24 is required to relate N_L to N_R.

Hiester et al. (1963, Eqn 16-54) have suggested that the resistances corresponding to pore diffusion, particle diffusion, film diffusion and axial dispersion are additive to a "fairly high degree of accuracy", as Van Deemter (Section 9-3) has suggested for gas chromatography. The results of HIXL suggest that the required relation for the number of reaction transfer units is:-

$$\frac{N}{N_R} = \frac{G}{b} + c\theta \qquad (9\text{-}18)$$

where $G = 1 + \xi$ for $\xi < 1$

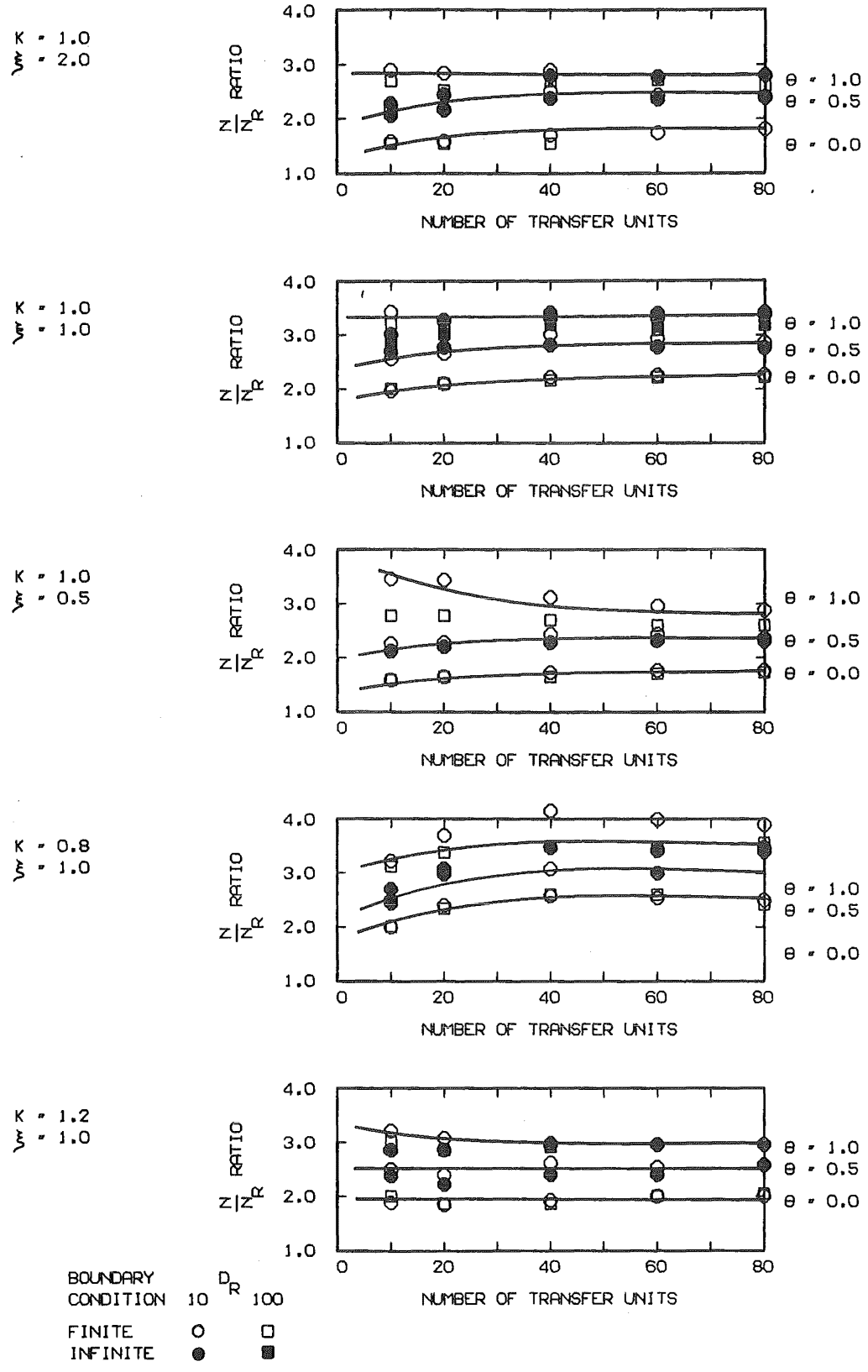
or $G = \frac{1 + \xi}{\xi}$ for $\xi > 1$

and c has a purpose analogous to that of b.

To determine the equivalent number of reaction transfer units, the results of HIXL have been treated in exactly the same way as experimental data. The breakthrough curve mid-point slope, $\left.\frac{\partial x}{\partial z}\right|_{x = 0.5}$, has been related to N_R (Figure 3-8). The resultant values of N/N_R have been listed in Table 9-4. Some details of the method used are included in Appendix 9E.

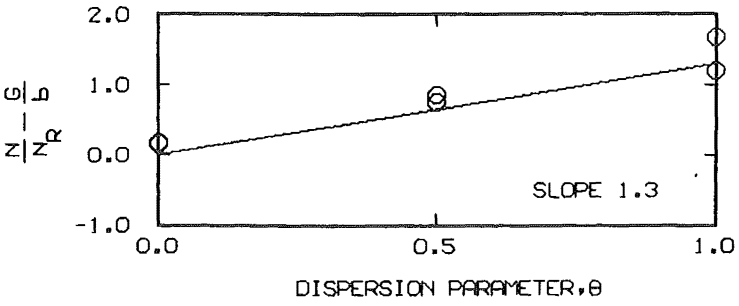
If the transfer unit ratio is plotted against the number of transfer units (Graph 9-18), the N/N_R values are sufficiently independent of N (particularly for more than 20 transfer units) for an average value to be taken.

Graph 9-19 shows these average values plotted in the form $\frac{N}{N_R} - \frac{G}{b}$ against θ. The slope of the best straight line fit

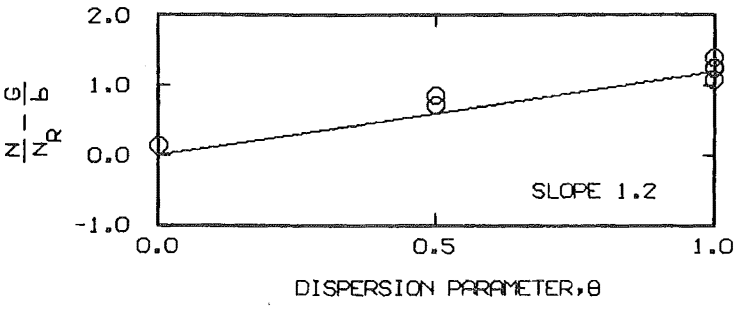


GRAPH 9-18. THE N/N_R RATIO DETERMINED FROM BREAKTHROUGH CURVE MID-POINT SLOPES.

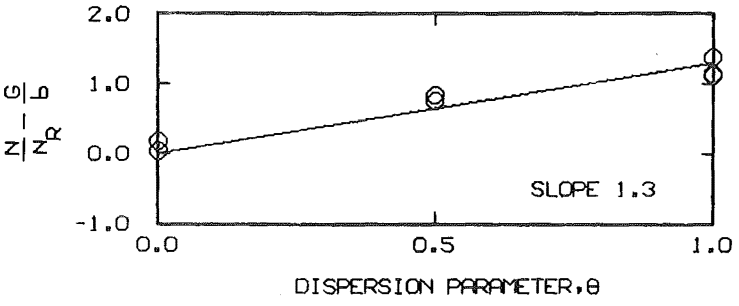
K = 1.0
ξ = 0.5



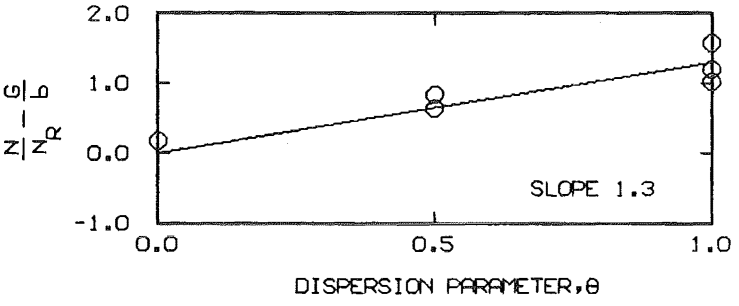
K = 1.0
ξ = 1.0



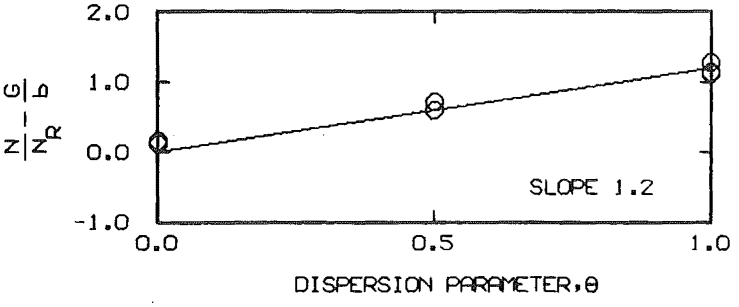
K = 1.0
ξ = 2.0



K = 0.8
ξ = 1.0



K = 1.2
ξ = 1.0



GRAPH 9-19. DETERMINATION OF THE CORRECTION FACTOR C (EQUATION 9-18).

in each case provides an estimate of c, and since the lines are straight, c is independent of the axial dispersion parameter.

For the small number of results available, there is no indication that c depends on the mechanism parameter, the distribution ratio, or the equilibrium ratio. The average value of c is 1.3, and it has been taken as constant with respect to D_R, N, θ, K and ξ.

Graphs 9-20 to 9-22 compare breakthrough curves predicted from Eqn 9-19 and the VHT method with HIXL and results from the BGP program. The agreement is good, as it should be since these results were among those used to generate Eqn 9-19.

The range of parameter values on which Eqn 9-19 was based is limited, especially for the separation factors used, which can probably be called "almost linear". Consequently, this approximate method must be considered tentative for very favourable or very unfavourable equilibrium, but it is simple to use and sufficiently accurate for the small axial dispersion effects in typical ion exchange beds.

Further work must be recommended to allow the behaviour of c to be more firmly established. However, this work should be done with a simpler model than HIXL, replacing the fickian particle diffusion equation by the linear form (Eqn 2-25b). By this means, the troublesome numerical differentiation would be avoided.

9-10 CONCLUSION

The hybrid computer model HIXL has been used to generate solutions to the fixed-bed ion exchange equations, including axial dispersion. Sufficient accuracy is difficult to achieve, but satisfactory results could be obtained, both to verify the method of computation and to provide a relationship between axial dispersion effects and the number of reaction transfer units. By this means, the Vermeulen-Hiester-Thomas breakthrough curve prediction method can be extended to conditions where the number of axial dispersion transfer units are few enough to be significant.

$\frac{N}{N_R}$ VALUES

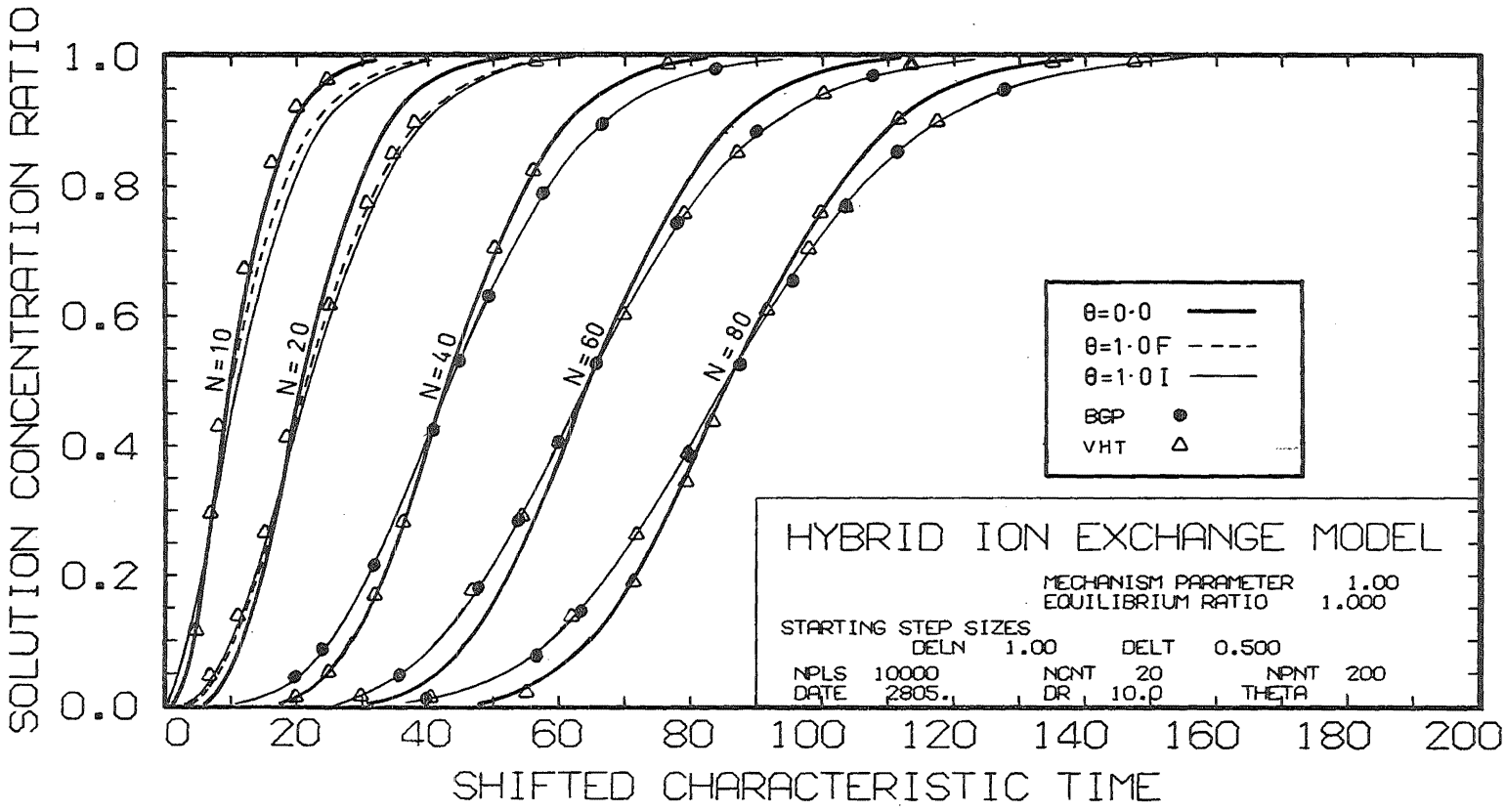
K = 1.0 ξ = 1.0

	θ	N=10	20	40	60	80	Average		θ	N=10	20	40	60	80	Average
ξ = 0.5	0.0	1.59	1.65	1.72	1.76	1.75	1.69	K = 0.8	0.0	2.00	2.41	2.58	2.55	2.50	2.41
		(1.59)	(1.65)	(1.65)	(1.71)	(1.72)	(1.66)			(2.00)	(2.35)	(2.61)	(2.61)	(2.42)	(2.40)
	0.5F	2.25	2.28	2.45	2.45	2.36	2.36		0.5F	2.50	2.99	3.08	-	-	2.86
	0.5I	2.12	2.20	2.28	2.32	2.31	2.25		0.5I	2.44	3.03	3.48	3.00	3.40	3.07
	1.0F	3.47	3.44	3.13	2.97	2.89	3.18		1.0F	3.23	3.70	4.17	4.00	3.90	3.80
		(2.78)	(2.78)	(2.70)	(2.61)	(2.61)	(2.70)			(3.13)	(3.39)	(3.51)	(3.49)	(3.56)	(3.42)
									1.0I	2.70	3.08	3.48	3.43	3.48	3.25
ξ = 1.0	0.0	1.96	2.11	2.22	2.26	2.25	2.14	K = 1.0	0.0	1.96	2.11	2.22	2.26	2.25	2.14
		(2.00)	(2.11)	(2.16)	(2.22)	(2.23)	(2.14)			(2.00)	(2.11)	(2.16)	(2.22)	(2.23)	(2.14)
	0.5F	2.70	2.78	3.03	2.94	2.86	2.86		0.5F	2.70	2.78	3.03	2.94	2.86	2.86
	0.5I	2.56	2.67	2.80	2.78	2.77	2.72		0.5I	2.56	2.67	2.80	2.78	2.77	2.72
	1.0F	3.45	3.28	3.42	3.41	3.42	3.40		1.0F	3.45	3.28	3.42	3.41	3.42	3.40
		(3.23)	(3.23)	(3.39)	(3.17)	(3.19)	(3.24)			(3.23)	(3.23)	(3.39)	(3.17)	(3.19)	(3.24)
	1.0I	3.03	3.28	3.33	3.33	3.38	3.27		1.0I	3.03	3.28	3.33	3.33	3.38	3.27
		(2.86)	(3.03)	(3.20)	(3.11)	(3.19)	(3.08)			(2.86)	(3.03)	(3.20)	(3.11)	(3.19)	(3.08)
ξ = 2.0	0.0	1.59	1.58	1.70	1.74	1.80	1.68	K = 1.2	0.0	1.89	1.85	1.92	2.01	2.00	1.93
		(1.54)	(1.54)	(1.54)	-	-	(1.54)			(2.00)	(1.87)	(1.86)	(2.00)	(2.05)	(1.96)
	0.5F	2.18	2.18	2.52	2.44	2.40	2.34		0.5F	2.50	2.41	2.63	2.55	2.58	2.53
	0.5I	2.06	2.17	2.38	2.37	2.38	2.27		0.5I	2.38	2.22	2.41	2.40	2.58	2.40
	1.0F	2.91	2.85	2.91	-	-	2.89		1.0F	3.23	3.08	2.97	-	-	3.09
		(2.70)	(2.53)	(2.70)	(2.72)	(2.61)	(2.65)			(3.03)	(2.86)	(2.93)	-	-	(2.94)
	1.0I	2.28	2.45	2.81	2.78	2.80	2.62		1.0I	2.86	2.86	2.99	2.97	2.96	2.93

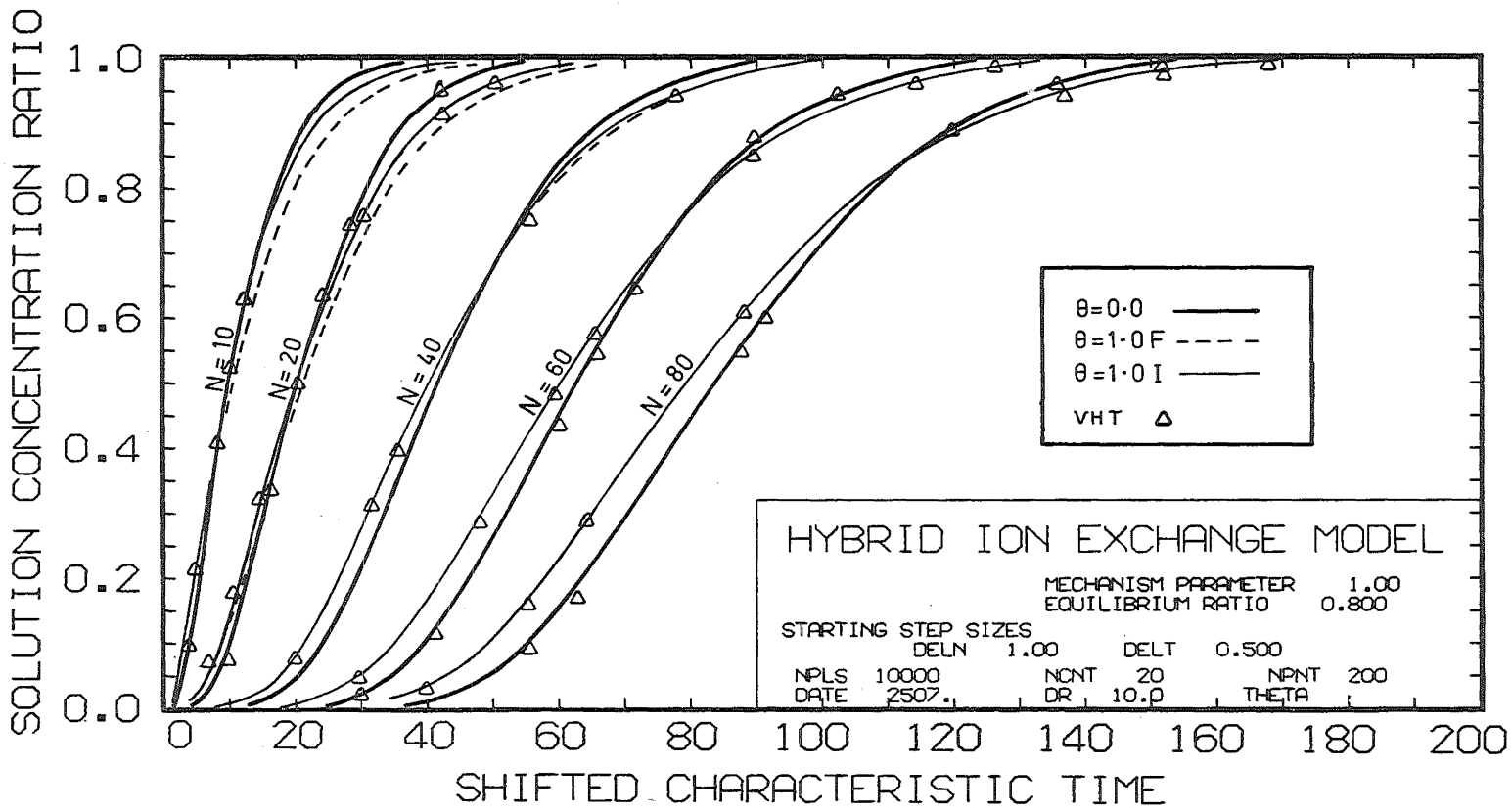
F indicates finite bed, I indicates infinite bed boundary condition.

All values are at D_R = 10.0, except those bracketed which are D_R = 100.0

TABLE 9-4 . N/N_R values for breakthrough curves from HIXL.



GRAPH 9-20. COMPARISON OF THE MODIFIED VHT METHOD WITH COMPUTED HIXL RESULTS.



GRAPH 9-21. COMPARISON OF THE MODIFIED VHT METHOD WITH COMPUTED HIXL RESULTS.

APPENDIX 9A

The BGP Program

Babcock, Green and Perry (1966) have extended the method developed by Rosen (Section 3-2) for linear equilibrium, film and fickian particle diffusion to include axial dispersion.

The program described here solves the equations derived by Babcock, but the necessary special attention has been paid to the evaluation of the infinite integral involved.

9A-1 The Infinite Integral

Points on the breakthrough curve are available from the infinite integral

$$x = \tfrac{1}{2} + \frac{2}{\pi} \int_0^\infty F(N_P, T_P, \theta, \xi, D_R, \lambda)\, d\lambda$$

where the integrand is a deceptively simple damped sinusoid:-

$$F = \frac{\exp(-A)\sin B}{\lambda}$$

But:-

$$A = \frac{N_p H_1}{5} + \frac{N_p \theta}{225}\left[C^2 - (3H_1)^2\right]$$

$$B = \frac{2}{15} T_p \lambda^2 - \frac{N_p}{5} \cdot H_2 + \frac{6\, N_p \theta H_1 C}{225}$$

$$C = \frac{2\lambda^2}{D_R} + 3H_2$$

$$H_1 = \left[\frac{H_{D1} + \frac{\xi}{5}(H_{D1}^2 + H_{D2}^2)}{H_{D3}}\right]$$

$$H_2 = \frac{H_{D2}}{H_{D3}}$$

$$H_{D3} = \left(1 + \frac{\xi}{5} H_{D1}\right)^2 + \left(\frac{\xi}{5} H_{D2}\right)^2$$

$$H_{D1} = \frac{\lambda(\sinh 2\lambda + \sin 2\lambda)}{\cosh 2\lambda - \cos 2\lambda}$$

$$H_{D2} = \frac{\lambda(\sinh 2\lambda - \sin 2\lambda)}{\cosh 2\lambda - \cos 2\lambda}$$

Rosen showed that there are useful limiting values on H_{D1}, H_{D2}

$\lambda < 0.4$	$\lambda > 5.0$
$H_{D1} = \frac{4\lambda^4}{45}$	$H_{D1} = \lambda - 1.0$
$H_{D2} = \frac{2\lambda^2}{3}$	$H_{D2} = \lambda$

9A-2 The Evaluation of the Integral

The integral is evaluated for λ increasing in steps, $\Delta\lambda$, until the integral has converged.

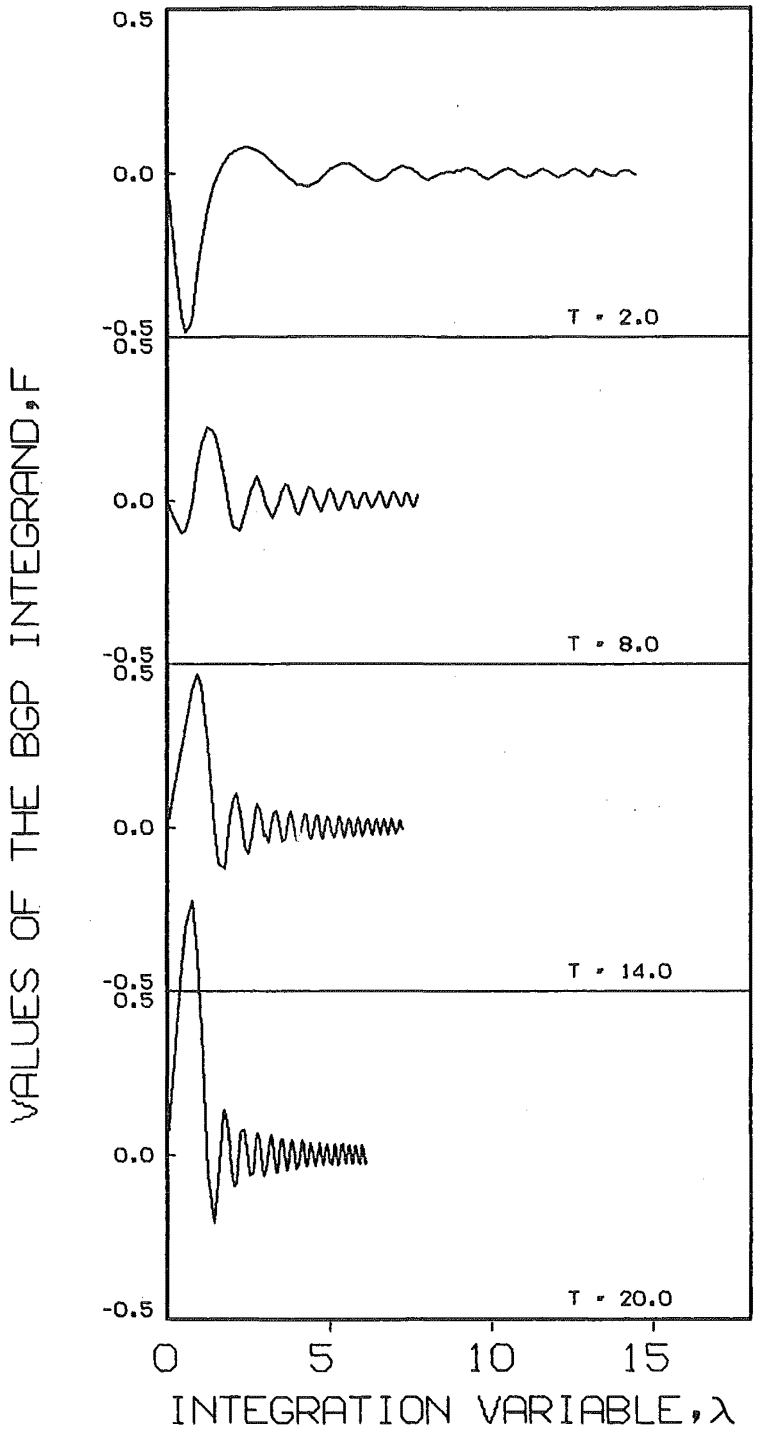
For each step, the area in that step is evaluated twice; with a Gaussian 3-point and a 6-point integration formula. If the relative error is acceptable then the estimate of the incremental area is added to the accumulated area. If the relative error is too small or too large, then the step size is doubled or halved, within limits imposed by the period of the damped sinusoid, F.

The convergence of this integral depends on the form of the integrand, F, either oscillatory or damped. If damped, the quadrature is not difficult. Graph 9A-1 shows the integrand when not damped.

If the convergence of this function is slow the integration must continue to large values of λ before the function becomes negligible. Massive computation would then be required because of the small step-size required by the high frequency of the oscillation.

The function F oscillates about zero. If the area under the curve up to some value of λ is $A(\lambda)$, then the value $A(\lambda)$ will be randomly distributed about $A(\infty)$. One value, $A(\lambda)$, before convergence, may be a good or bad estimate of $A(\infty)$, but a series of values of $A(\lambda)$ can be considered as a sequence of estimates of $A(\infty)$, which, when appropriately smoothed, gives a standard deviation small enough for the smoothed value to be accepted as $A(\infty)$, well before convergence.

First-order exponential smoothing has been used (Brown, 1962) according to:-



GRAPH 9A-1. THE OSCILLATION OF THE BGP INTEGRAND.

$$S_n = a\, S_{n-1} + (1 - a) A_n$$

where a is the smoothing factor

S_n is the smoothed value, after n samples

and A_n is the nth sample.

The standard deviation of the smoothed output is $\frac{\sqrt{SS_n}}{m}$ where

SS_n is the smoothed sum of squares after n samples:-

$$SS_n = a\, SS_{n-1} + (1 - a)(S_n - A_n)^2$$

and m the equivalent number of data points:-

$$m = \frac{1 + a}{1 - a}$$

The integration continues until

(a) The amplitude of the function is negligible

(b) For an oscillating integral, the smoothed standard deviation is acceptable (less than 0.0002), or

(c) For a damped integral, the unsmoothed standard deviation is acceptable.

The value chosen for the smoothing factor was 0.6, as this gave the best compromise (Graph 9A-2) between inadequate damping (a = 0.5) and sluggish response (a = 0.67).

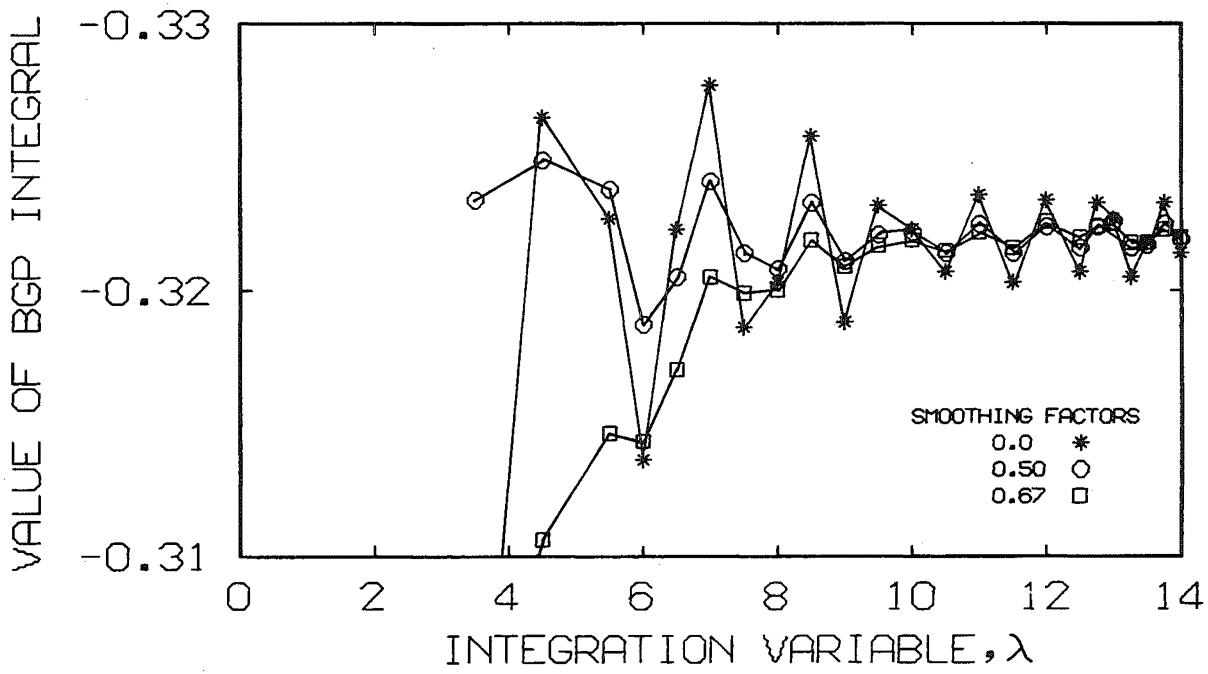
9A-3 BGP Verification

Table 9A-1 compares results from BGP with a selection of Rosen's results. The agreement generally between the two corresponds to the uncertainty in the computed values, 0.002 to 0.02 for Rosen and 0.001 for BGP.

Verification for axial dispersion was completed by a hand calculation.

Convergence was slowest for short beds. Babcock reported inaccuracy for N_p less than 10. This integration method has had no such difficulty.

On average, integration continued to λ values of about 3 to 5 before an acceptable area estimate was obtained.



GRAPH 9A-2. SELECTION OF THE SMOOTHING FACTOR FOR BGP INTEGRATION.

```
0001            FUNCTION BGP(ZETA,N,THETA,DIS,T)
                C
                C     BABCOCK-GREEN-PERRY LONGITUDINAL DISPERSION PROGRAM
                C
                C
                C   PURPOSE
                C
                C
                C     TO COMPUTE BREAKTHROUGH CURVES USING THE BGP EQUATIONS,ONLY FOR
                C     LINEAR EQUILIBRIUM,BUT INCLUDING AXIAL DISPERSION IF REQUIRED
                C
                C   USAGE
                C
                C     X=BGP(ZETA,N,THETA,DIST,T)
                C
                C   PARAMETERS
                C
                C     X         SOLUTION CONCENTRATION RATIO
                C     ZETA      MECHANISM PARAMETER
                C     N         NUMBER OF TRANSFER UNITS ON CONTROLLING SIDE
                C     DIST      DISTRIBUTION RATIO
                C     T         CHARACTERISTIC TIME
                C
                C   SUBPROGRAMS REQUIRED
                C
                C     F         INTEGRAND CALCULATION
                C
                C
0002            COMMON A,B,DELL,NU,DIST,TP,NP,ETA
0003            REAL K,NP,NL,MECP,LAMDA,NU,N,SAVE(10)
0004            LOGICAL DEBUG
                C
                C
                C
                C   DEBUG=TRUE FOR INTERMEDIATE PRINTOUT FOR VERIFICATION
                C
                C                                                    .EURT.=GUBED
0005            DEBUG=.FALSE.
0006            DIST=DIS
0007            IF(DIST.EQ.0.0)DIST=1.0
0008            DELL=1.0
0009            IF(ZETA.GT.1.0)DELL=1.0/ZETA
0010            ALFA=.6
0011            ALFAM=1.-ALFA
0012            EPSA=0.01
0013            EPSI=0.001
                C
0014            ETA=THETA
0015            IF(ZETA.GT.1.0)ETA=ZETA*THETA
```

```
0016              NP=N
0017              IF(ZETA.GT.1.0)NP=ZETA*N
0018              NU=ZETA/5.0
0019              TP=NP/N*T
                  C
                  C     N     NUMBER OF TRANSFER UNITS ON CONTROLLING SIDE
                  C     NP    NUMBER OF PARTICLE SIDE TRANSFER UNITS
                  C     ETA   NP/NL,   NL   NUMBER OF AXIAL TRANSFER UNITS
                  C     ZETA  MECHANISM PARAMETER,NP/NF
                  C     T     CHARACTERISTIC TIME,Z*N
                  C     TP    CPARACTERISTIC TIME,Z*NP
                  C     DIST  Q/&/CO
                  C     DELL INITIAL STEP SIZE IN LAMDA,ADAPTIVE
                  C     EPSA  AMPLITUDE LIMIT FOR END OF INTEGRATION
                  C     EPSI  RELATIVE ACCURACY OF INTEGRATION
0020              IF(DEBUG)WRITE(6,117)ZETA,N,THETA,DIST,T,ETA,TP,NP,EPSA,EPSI
0021            117 FORMAT('8'/'1'T5'ZETA'T19'N'T29'THETA'T44'DIST'T58'T'
                   1T70'ETA'T84'TP'T97'NP'T108'EPSA'T121'EPSI'  /' '10G13.5/' '22('---
                   2---')/'    LAMDA'T14'AREA'T27'S'T38'A3'T49'A6'T59'AMP'T69'PERIOD'
                   6T82'P1'T93'P2'T104'P3'T115'SD'T125'UNSD')
                  C
                  C     INITIALISE FOR EACH T,X POINT
                  C
0022              2 LAMDA=0.0
0023                AREA=0.0
0024                S=0.0
0025                SS=0.0
0026                KOUNT=0
0027                NSDP=3
0028                DO270I=1,5
0029                SAVE(I)=0.0
0030            270 CONTINUE
                  C
                  C     LOOP FOR INCREASING LAMDA
                  C
0031             51 C=LAMDA+0.5*DELL
0032                D=.774597*DELL*.5
0033                D1=C-D
0034                D3=C+D
0035                P1=F(D1)
0036                P2=F(C)
0037                P3=F(D3)
0038                A3=(5.0*(P1+P3)+8.0*P2)/9.0
0039                A3=A3*DELL*0.5
                  C
                  C     TEST FOR SMALL AREA
                  C
0040              5 IF(A3.GT.0.0005) GO TO 3
0041                A6=A3
```

```
0042                GO TO 4
0043              3 D1=.238619*DELL*.5
0044                D2=.661209*DELL *.5
0045                D3=.932470*DELL  *.5
0046                A6=.467914*(F(C+D1)+F(C-D1))
                   1       +.360762*(F(C+D2)+F(C-D2))
                   1       +.171324*(F(C+D3)+F(C-D3))
0047                A6=A6*DELL*.5
0048                E=ABS((A6-A3)/A6)
0049                IF(E.GT.EPSI)GOTO17
0050              4 LAMDA=LAMDA+DELL
0051                AREA=AREA+A6
0052                AMP=EXP(-A)/LAMDA
0053                PERIOD=6.28319*LAMDA/B
                C
                C       SHOULD THE LAMDA STEP SIZE BE DOUBLED
                C
0054                IF(E.LT.EPSI/100.0.AND.DELL.LT.2.*LAMDA/B)DELL=2.*DELL
                C
                C
                C       GET STANDARD DEVIATION OF UNSMOOTHED AREA
                C
0055                KOUNT=KOUNT+1
0056                IF(KOUNT.GT.NSDP)KOUNT=  NSDP
0057                NSDM=NSDP-1
0058                DO271I=1,NSDM
0059                SAVE(I)=SAVE(I+1)
0060              271 CONTINUE
0061                SAVE(NSDP )=AREA
0062                IF(KOUNT.EQ.1)GOTO57
0063                SUM=0.0
0064                IFL=NSDP+1-KOUNT
0065                DO272I=IFL,NSDP
0066                SUM=SUM+SAVE(I)
0067              272 CONTINUE
0068                XB=SUM/KOUNT
0069                SUM=0.0
0070                DO273I=IFL,NSDP
0071                DF=SAVE(I)-XB
0072                SUM=SUM+DF*DF
0073              273 CONTINUE
0074                UNSD=SUM/(KOUNT-1)
0075                UNSD=SQRT(UNSD)
                C
                C       EVALUATE THE SMOOTHED STANDARD DEVIATION
                C
                C  S=SMOOTHED ESTIMATE OF AREA
                C
                C
```

```
0076              S=ALFA*S+ALFAM*AREA
0077              SS=ALFA*SS+ALFAM*(AREA-S)**2
0078              SD=SQRT(SS)*ALFAM/(1.+ALFA)
0079           57 IF(DEBUG)WRITE(6,118)LAMDA,AREA,S,A3,A6,AMP,PERIOD,P1,P2,P3,SD,
                  1UNSD
0080          118 FORMAT(' '12G11.4)
0081              IF(KOUNT.EQ.1)GOTO51
0082              IF(LAMDA.LT.3.0)GOTO51
0083              IF(LAMDA.GE.50.0)GOTO7
0084              IF(AMP.LT.1.0E-6)GOTO7
0085              IF(UNSD.LT.0.0002)GOTO7
0086              IF(SD.GT..0002)GOTO51
0087            7 CONTINUE
                C
                C     EVALUATE X
                C
0088              UNSMX=0.5+2.0/3.14159256*AREA
0089              SMX=.5+2./3.14159256*S
                C
                C     WRITE FUNCTION VALUES,T AND X
                C
0090              IF(DEBUG)WRITE(6,102)T,UNSMX,SMX
0091          102 FORMAT(/' T,X(UNSMOOTHED AND SMOOTHED)'3G15.5//)
0092              BGP=UNSMX
0093              IF(UNSD.GT.SD)BGP=SMX
0094              IF(UNSD.LT.SD)SD=UNSD
0095              ESTE=2.5*SD
0096              IF(ESTE.GT.0.001)WRITE(6,103)
0097          103 FORMAT(' BGP ERROR MAY BE LARGE')
0098              RETURN
                C
                C   HALVE STEP-SIZE
                C
0099           17 DELL=.5*DELL
0100              IF(DELL.GT.0.0001)GOTO51
0101              WRITE(6,191)
0102          191 FORMAT(' DELL TOO SMALL')
0103              BGP=-0.00001
0104              RETURN
0105              END
```

```
0001            FUNCTION F(LAMDA)
                C
                C   PURPOSE
                C
                C     TO CALCULATE THE VALUE OF THE BGP INTEGRAND,ARGUMENT LAMDA
                C
0002            REAL LAMDA,NU,NP
0003            COMMON A,B,DELL,NU,DIST,TP,NP,ETA
0004            LOGICAL DEBUG
0005            DEBUG=.FALSE.
0006            P=2.0*LAMDA
0007            IF(LAMDA.LT.5.0) GO TO 6
                C
                C     LIMIT IF LAMDA LARGE
                C
0008            HD1=LAMDA-1.0
0009            HD2=LAMDA
0010            GO TO 9
0011          6 IF(LAMDA-0.4) 7,8,8
                C
                C     USE ROSEN'S LIMIT IF LAMDA SMALL
                C
0012          7 HD2=2.0/3.0*LAMDA*LAMDA
0013            HD1=HD2*HD2/5.0
0014            GO TO 9
                C
                C     LAMDA LARGER THAN 0.1
                C
0015          8 CMC=COSH(P)-COS(P)
0016            SH=SINH(P)
0017            SI=SIN(P)
0018            HD1=LAMDA*(SH+SI)/CMC-1.0
0019            HD2=LAMDA*(SH-SI)/CMC
0020          9 HD3=(1.0+NU*HD1)**2+(NU*HD2)**2
0021            H1=(HD1+NU*(HD1*HD1+HD2*HD2))/HD3
0022            H2=HD2/HD3
0023            H3=2.0/DIST*LAMDA*LAMDA+3.0*H2
0024            H4=NP*ETA/225.0
0025            A=NP*H1/5.0+H4*(H3*H3-9.0*H1*H1)
0026            B=2.0/15.0*TP*LAMDA*LAMDA-NP/5.0*H2+6.0*H4*H1*H3
0027            F=EXP(-A)*SIN(B)/LAMDA
0028            IF(DEBUG)WRITE(6,100)LAMDA,HD1,HD2,HD3,H1,H2,H3,A,B,F,DELL
0029        100 FORMAT(' '11G12.4)
0030            RETURN
0031            END
```

APPENDIX 9B

THE NORMALISATION OF THE HIXL EQUATIONS

The equations of the HIXL model (listed in Table 9-1) have been normalised with the following substitutions:-

$$N_p = \frac{Q\ k_p\ z}{C_o v} \qquad N_f = \frac{Q\ k_f\ z}{C_o v}$$

$$S_p = k_p t \qquad S_f = k_f t$$

$$R = \frac{r}{a}$$

or, in general:-

$$N = \frac{Q\ k\ z}{C_o v} \qquad S = kt \qquad R = \frac{r}{a}$$

The dependent variables are:-

$$x = x(N,S)$$

$$\bar{y} = \bar{y}(N,S)$$

$$y = y(N,S,R)$$

The non-zero differentials of the system are:-

$$\frac{\partial N}{\partial z} = \frac{Qk}{C_o v} \qquad \frac{\partial S}{\partial t} = k \qquad \frac{\partial R}{\partial r} = \frac{1}{a}$$

$$\frac{\partial x}{\partial z} = \frac{Qk}{C_o v} \cdot \frac{\partial x}{\partial N} \qquad \frac{\partial x}{\partial t} = k \cdot \frac{\partial x}{\partial S} \qquad \frac{\partial \bar{y}}{\partial t} = k \cdot \frac{\partial \bar{y}}{\partial S}$$

$$\frac{\partial y}{\partial t} = k \cdot \frac{\partial y}{\partial S} \qquad \frac{\partial y}{\partial r} = \frac{1}{a} \cdot \frac{\partial y}{\partial R}$$

$$\frac{\partial^2 x}{\partial z^2} = \left(\frac{Qk}{C_o v}\right)^2 \cdot \frac{\partial^2 x}{\partial N^2} \qquad \frac{\partial^2 y}{\partial r^2} = \frac{1}{a^2} \cdot \frac{\partial^2 y}{\partial R^2}$$

9B-1 The Solution Mass Balance

Substituting these derivatives into Eqn 9-1 gives:-

$$\frac{N}{N_L} \cdot \frac{\partial^2 x}{\partial N^2} = \frac{\partial x}{\partial N} + \frac{\partial \bar{y}}{\partial S} + \frac{\varepsilon C_o}{Q} \cdot \frac{\partial x}{\partial S}$$

or:-

$$\theta \frac{\partial^2 x}{\partial N^2} = \frac{\partial x}{\partial N} + \frac{\partial \bar{y}}{\partial S} + \frac{1}{D_R} \cdot \frac{\partial x}{\partial S} \qquad (9B\text{-}1)$$

This equation applies to either computational basis.

9B-2 The Particle Mass Balance

Eqn 9-2 is

$$\frac{\partial \bar{y}}{\partial t} = \frac{6 D_p}{d_p} \frac{\partial y}{\partial r}\bigg|_{r=d_p/2}$$

and becomes

$$\frac{\partial \bar{y}}{\partial S} = \frac{12 D_p}{k d_p^2} \frac{\partial y}{\partial R}\bigg|_{R=1}$$

since $k_p = \dfrac{60 D_p}{d_p^2}$

$$\frac{\partial \bar{y}}{\partial S} = \frac{k_p}{5k} \frac{\partial y}{\partial R}\bigg|_{R=1} = \frac{\sigma}{5} \frac{\partial y}{\partial R}\bigg|_{R=1} \qquad (9B\text{-}2)$$

For a particle-phase basis, $k = k_p$ and $\sigma = \dfrac{k_p}{k_p} = 1.0$

For a solution-phase basis, $k = k_f$ and $\sigma = \dfrac{k_p}{k_f} = \xi$

9B-3 The Solution Rate Equation

From Eqn 9-3

$$\frac{\partial \bar{y}}{\partial t} = k_f (x - x^*)$$

and hence

$$\frac{\partial \bar{y}}{\partial S} = \frac{k_f}{k} (x - x^*) = \rho (x - x^*) \qquad (9B\text{-}3)$$

For a particle-phase basis, $k = k_p$ and $\rho = \dfrac{k_f}{k_p} = \dfrac{1}{\xi}$

For a solution-phase basis, $k = k_f$ and $\rho = \frac{k_f}{k_f} = 1.0$.

9B-4 The Particle Rate Equation

Substituting derivatives into Eqn 9-4

$$\frac{\partial y}{\partial S} = \frac{k_p}{15k} \cdot \left(\frac{\partial^2 y}{\partial R^2} + \frac{2}{R}\frac{\partial y}{\partial R}\right) \qquad (9B\text{-}4)$$

For a particle phase basis, $k = k_p$ and $\sigma = \frac{k_p}{k_p} = 1.0$

For a solution phase basis, $k = k_f$ and $\sigma = \frac{k_p}{k_f} = \xi$

in agreement with section 9B-2.

9B-5 Initial and Boundary Conditions

The initial conditions used with HIXL are the same as those of HIXM. The boundary condition at the top of the bed for a finite column (Eqn 9-6a):-

$$x = x_o + \frac{\epsilon E_A}{v} \cdot \frac{\partial x}{\partial z} \quad \text{for } z = 0,\ t > 0$$

becomes, when written in terms of the normalised variables:-

$$x = x_o + \frac{N}{N_L}\frac{\partial x}{\partial N}$$

$$= x_o + \theta\frac{\partial x}{\partial N} \qquad \text{for } N = 0,\ S > 0. \qquad (9B\text{-}5)$$

APPENDIX 9C

THE ANALOG PROGRAMMING FOR HIXL

The complete analog computer program for HIXL is shown in Figure 9C-1 and Table 9C-1 contains the potentiometer settings.

9C-1 The Solution Mass Balance

The solution mass balance (Eqn 9-9) is used in the form:-

$$\frac{dx}{dS} = BD_R \left(\theta \frac{\partial^2 x}{\partial N^2} - \frac{\partial x}{\partial N} - \frac{\partial \bar{y}}{\partial T}\right) \qquad (9C\text{-}1)$$

and integrated to give $x_{N+\Delta N}$ in the first cell or $x_{N+2\Delta N}$ in the second (Figure 9C-2) where B is a time scale factor.

The second derivative is calculated for both cells:-

$$\frac{\partial^2 x}{\partial N^2} = \frac{x_{N+2\Delta N} - 2x_{N+\Delta N} + x_N}{(\Delta N)^2} + O(\Delta N)^3 \qquad (9C\text{-}2)$$

The first derivative, $\frac{\partial x}{\partial N}$, is calculated for each cell using the same differential approximations as HIXM:-

First cell
$$\left.\frac{\partial x}{\partial N}\right|_{N+\Delta N} = \frac{x_{N+2\Delta N} - x_N}{2\Delta N} \qquad (9C\text{-}3)$$

Second cell
$$\left.\frac{\partial x}{\partial N}\right|_{N+2\Delta N} = \frac{3x_{N+2\Delta N} - 4x_{N+\Delta N} + x_N}{2\Delta N} \qquad (9C\text{-}4)$$

The odd gains of 11 and 21 have been introduced to improve accuracy by preventing any potentiometers being required to set to values near 1.0, impossible because of loading errors.

9C-2 Interfacial Concentrations

The solution interfacial concentration is calculated from the solution rate equation (Eqn 9-11):-

$$x^* = x - \frac{1}{\rho} \cdot \frac{d\bar{y}}{dS}$$

The particle interfacial concentration is calculated from the equilibrium relation (Eqn 9-13)

$$y^* = \frac{Gx^*}{\frac{G}{K}(1 - x^*) + Gx^*}$$

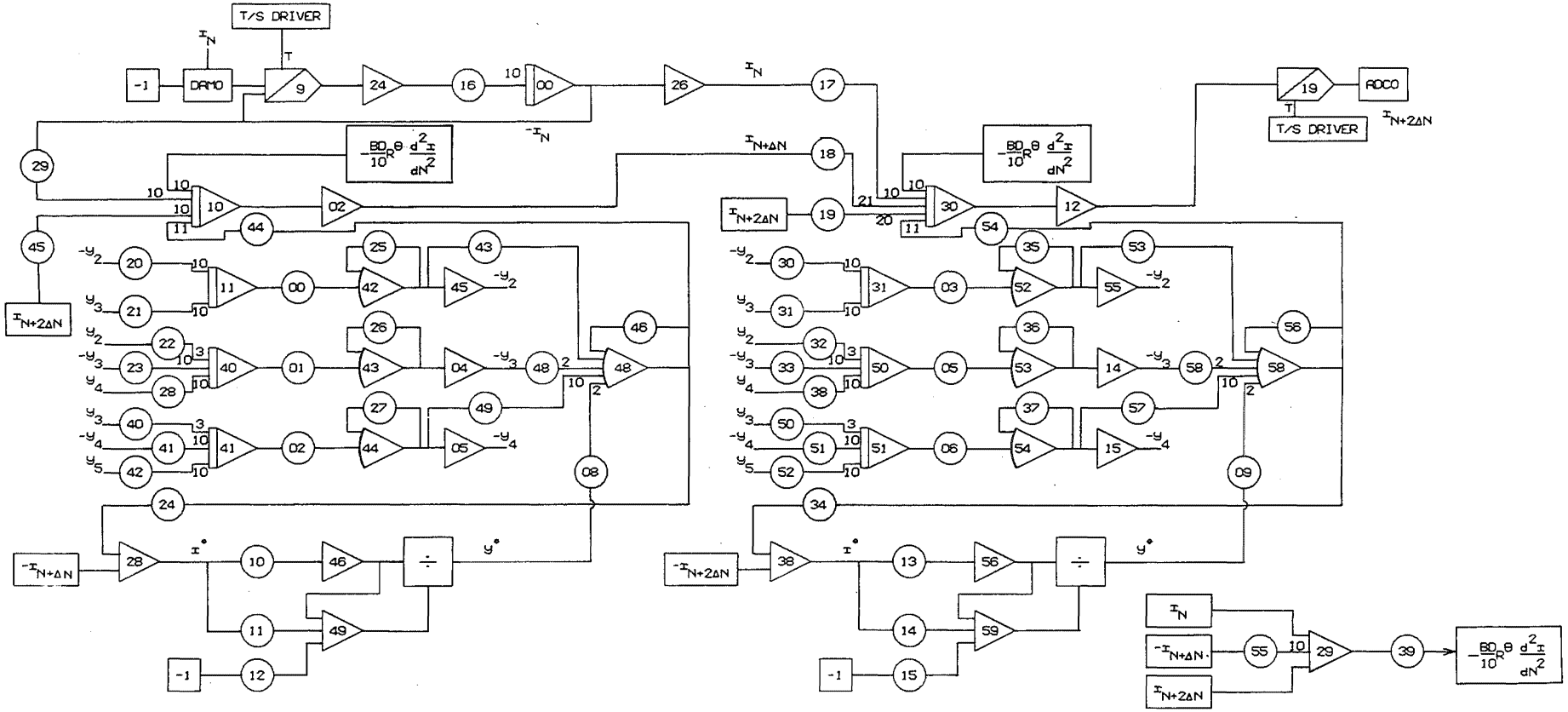


FIGURE 9C-1. ANALOG COMPUTER PROGRAMMING FOR HIXL.

where G = K for K < 1.0

G = 1.0 for K ≥ 1.0.

This relation is similar to that used in HIXM, in that all values of the separation factor can be used without repatching, but differs in that y*, and not x*, is required. The factors of 0.95 included in Figure 9C-4 help accuracy in that no potentiometers are set to 0.9999 and loading errors are avoided.

9C-3 The Calculation of Rate

The particle concentrations are calculated with four radial elements by integrating (Eqns 8-3):-

$$\frac{dy_2}{dS} = B\left(\frac{32\sigma}{15} y_3 - \frac{32\sigma}{15} y_2\right)$$

$$\frac{dy_3}{dS} = B\left(\frac{8\sigma}{5} y_4 - \frac{32\sigma}{15} y_3 + \frac{8\sigma}{15} y_2\right)$$

$$\frac{dy_4}{dS} = B\left(\frac{64\sigma}{45} y_5 - \frac{32\sigma}{15} y_4 + \frac{32}{45} y_3\right)$$

where B is a time scale factor. The resin concentration gradient at the surface of the particle is found from a differentiation approximation (Goodwin, 1961, page 67)

$$\left.\frac{\partial y}{\partial R}\right|_{R=1} = \frac{\left(\nabla + \frac{\nabla^2}{2} + \frac{\nabla^3}{3} + \frac{\nabla^4}{4} \ldots\right) y_5}{\Delta R}$$

$$= \frac{2}{3}(11y_5 - 18y_4 + 9y_3 - 2y_2)$$

The rate, $\frac{d\bar{y}}{dS}$, is calculated (Figure 9C-5) from particle mass balance equation (Eqn 9-10)

$$\frac{\partial \bar{y}}{\partial S} = \frac{\sigma}{5}\left.\frac{\partial y}{\partial R}\right|_{R=1}$$

$$= \frac{2\sigma}{15}(11y_5 - 18y_4 + 9y_3 - 2y_2)$$

Potentiometer Number	0	1	2	3	4	5	6	7	8	9
00	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.1393	0.1393
10	.95G	$\frac{.95\ G}{K}$	$\frac{.95\ G}{K}$	.95G	$\frac{.95\ G}{K}$	$\frac{.95\ G}{K}$	$\frac{ITSF}{10\ MST}$	$\frac{1}{2\Delta N}\ \frac{BD}{10}$	$\frac{2}{\Delta N}\ \frac{BD}{21}$	$\frac{.75}{\Delta N}\ \frac{BD}{10}$
20	$\frac{32B}{150}$	$\frac{32B}{150}$	$\frac{8B}{45}$	$\frac{32B}{150}$	$\frac{1}{\rho}$	$\frac{.95}{\sigma}$	$\frac{.95}{\sigma}$	$\frac{.95}{\sigma}$	.16B	$\frac{1}{2\Delta N}\ \frac{BD}{10}$
30	$\frac{32B}{150}$	$\frac{32B}{150}$	$\frac{8B}{45}$	$\frac{32B}{150}$	$\frac{1}{\rho}$	$\frac{.95}{\sigma}$	$\frac{.95}{\sigma}$	$\frac{.95}{\sigma}$	.16B	$\frac{\theta}{\Delta N^2}\ \frac{BD}{10}$
40	$\frac{32B}{135}$	$\frac{32B}{150}$	$\frac{64B}{450}$	.2533	$\frac{BD}{11}$	$\frac{1}{2\Delta N}\ \frac{BD}{10}$	$\frac{.95}{\sigma}$	.2280	.57	-
50	$\frac{32B}{135}$	$\frac{32B}{150}$	$\frac{64B}{450}$	.2533	$\frac{BD}{11}$	0.2	$\frac{.95}{\sigma}$	.2280	.57	0.5

TABLE 9C-1. Potentiometer settings for the hybrid computer model HIXL.

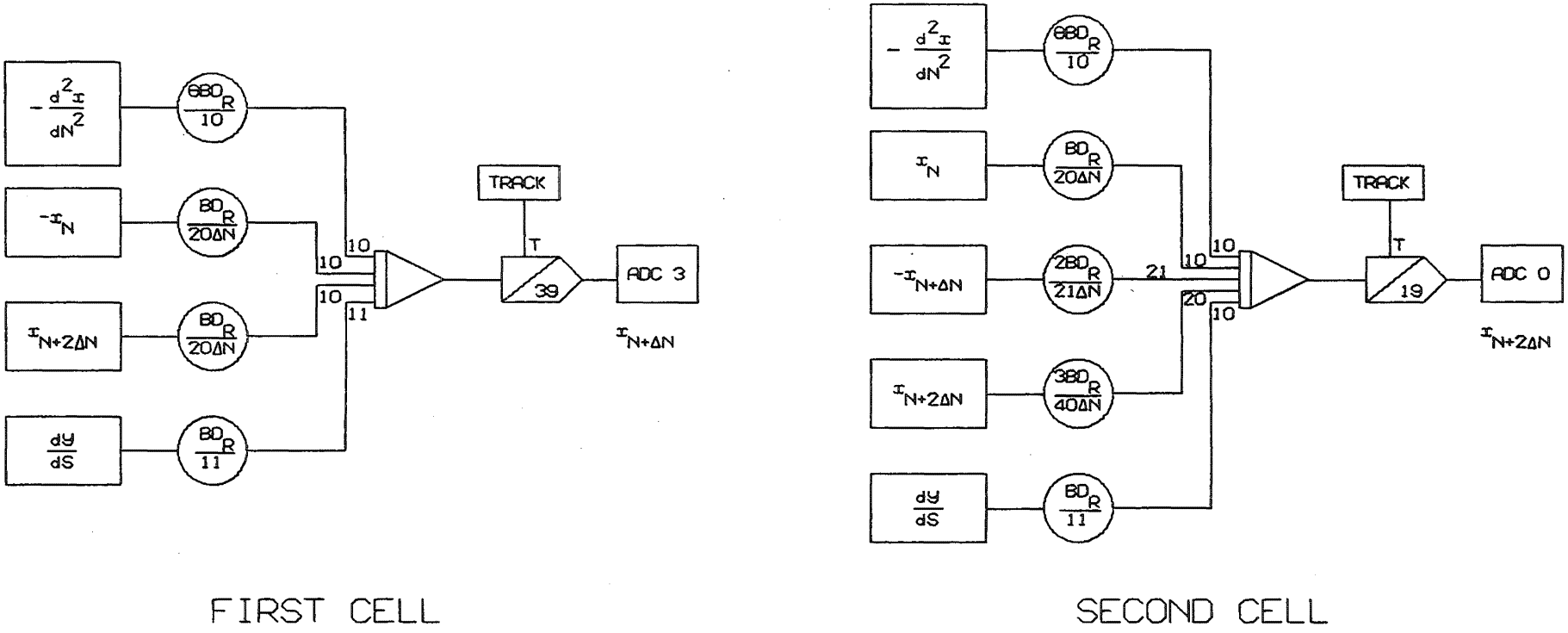


FIGURE 9C-2. ANALOG PROGRAMMING - BREAKTHROUGH CURVE GENERATION.

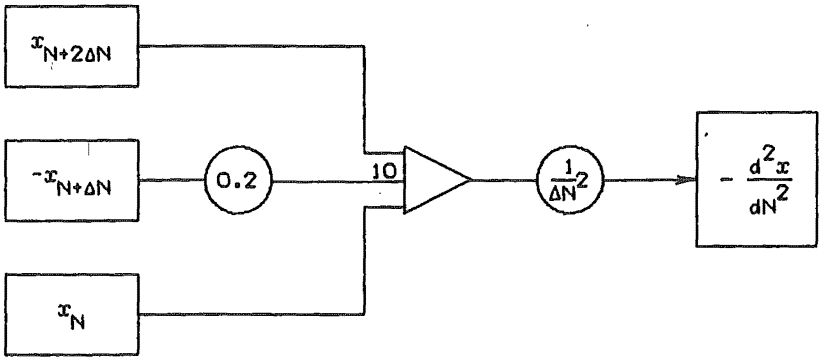


FIGURE 9C-3. ANALOG PROGRAMMING FOR HIXL - SECOND DERIVITIVE GENERATION.

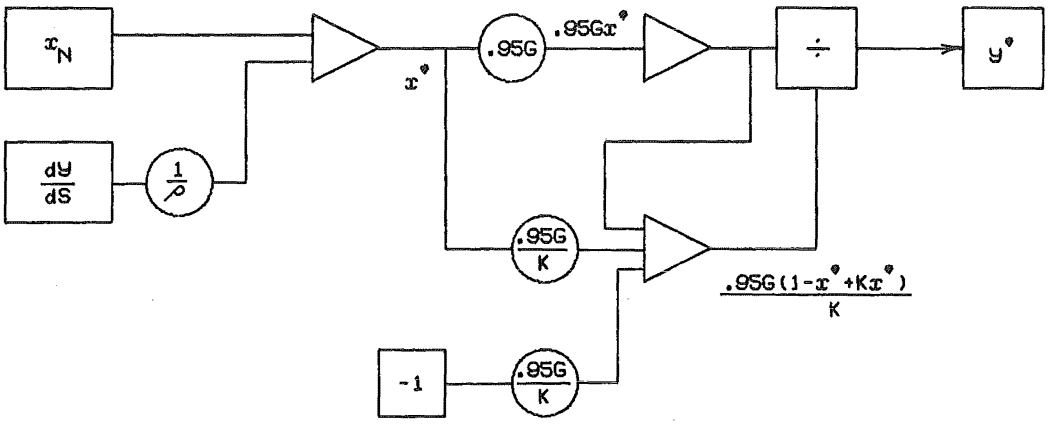


FIGURE 9C-4. ANALOG PROGRAMMING FOR HIXL - INTERFACIAL CONCENTRATIONS.

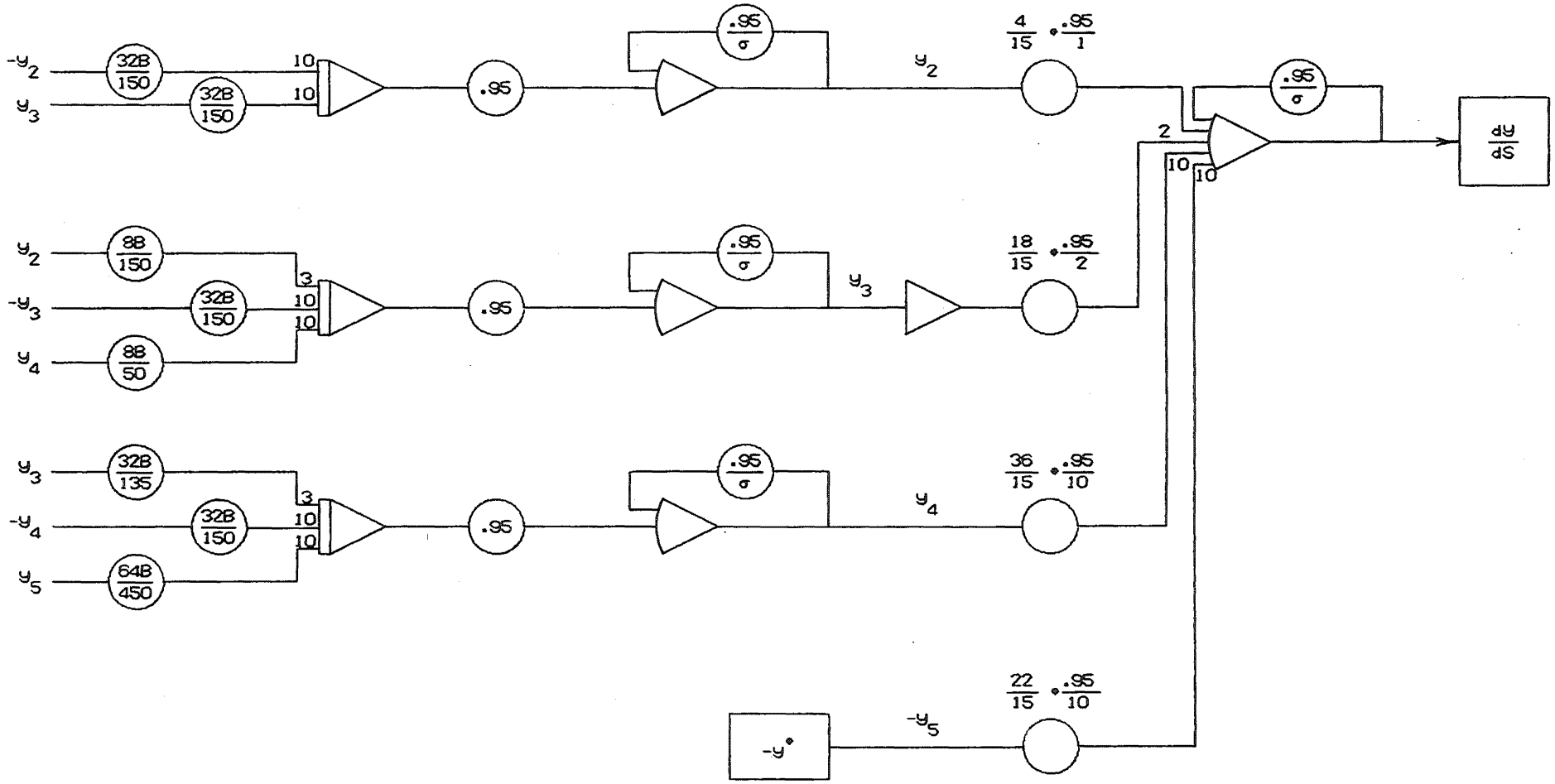


FIGURE 9C-5. ANALOG PROGRAMMING FOR HIXL - RATE CALCULATION.

APPENDIX 9D

ACCURACY IN HIXL

Early results from HIXL (such as shown in Graph 9-3) failed to attain the correct steady-state solution concentration equal to the feed concentration.

If a stable, non-oscillating steady-state solution exists for the fixed-bed ion exchange equations (and it must if the model is a reasonable expression of the physical reality), then all derivatives must be zero. This implies that the inputs to all analog integrators must be zero. The two main integrators of the analog portion of HIXL are numbered 10 and 30 in Figure 9C-1. The conditions for these integrators to be at steady-state are:-

$$-\frac{1}{2\Delta N}x_N + \frac{1}{2\Delta N}x_{N+\Delta N} + \left.\frac{d\bar{y}}{d\bar{s}}\right|_{N+\Delta N} = 0 \qquad (9D\text{-}1)$$

$$\frac{1}{2\Delta N}x_N - \frac{2}{\Delta N}x_{N+\Delta N} + \frac{1.5}{\Delta N}x_{N+2\Delta N} + \left.\frac{d\bar{y}}{d\bar{s}}\right|_{N+2\Delta N} = 0 \qquad (9D\text{-}2)$$

assuming that $\theta = 0$ (the steady-state inaccuracy problem occurred for all values of θ). The steady-state values of $x_{N+\Delta N}$, $x_{N+2\Delta N}$ are:-

$$x_{N+\Delta N} = x_N - \frac{3}{2}\cdot\Delta N \cdot \left.\frac{d\bar{y}}{d\bar{s}}\right|_{N+\Delta N} + \frac{\Delta N}{2}\cdot\left.\frac{d\bar{y}}{d\bar{s}}\right|_{N+2\Delta N}$$

$$x_{N+2\Delta N} = x_N - 2\cdot\Delta N \cdot \left.\frac{d\bar{y}}{d\bar{s}}\right|_{N+\Delta N}$$

Interestingly, the steady-state value of $x_{N+2\Delta N}$ depends only on the values from the first cell, while the steady-state value of $x_{N+\Delta N}$ depends on both. Accuracy in the first cell is therefore more important because only the second profile, $x_{N+2\Delta N}$, is retained for further use.

Both steady-state breakthrough curve values depend directly on the input profile, x_N, and any input error will not be attenuated.

Further, the steady-state value of $x_{N+2\Delta N}$ depends directly on the calculation of the rate in the first cell, $\left.\frac{d\bar{y}}{d\bar{s}}\right|_{N+\Delta N}$. Any error in this quantity, formed by a numerical differentiation, will be magnified (at least twice) by the factor $2\Delta N$.

The error involved in the calculation of a rate, $\frac{d\bar{y}}{ds}$, can be estimated. Figure 9D-1 (a portion of Figure 9C-5) shows the analog patching involved. If the error in each y value is 0.0002, with the same error in each potentiometer setting, then the uncertainty ΔR in the calculation of the rate, R, at steady-state is (for $\sigma = 1.0$):-

$$\Delta R = \frac{\sigma}{.95} [\Delta(y_2 \times C_1) + 2.\Delta(y_3 \times C_2) + 10.\Delta(y_4 \times C_3) + 10.\Delta(y_5 \times C_4)]$$

$$= \frac{\sigma}{.95} [1.0(\Delta C_1 + 2.\Delta C_2 + 10.\Delta C_3 + 10.\Delta C_4)$$

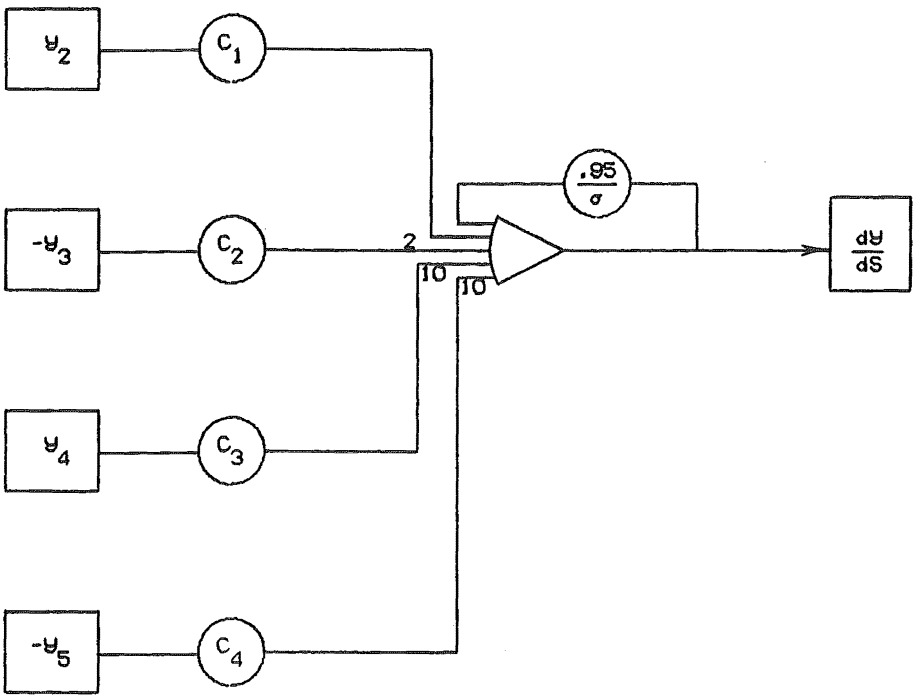
$$+ 0.0002(C_1 + 2*C_2 + 10*C_3 + 10*C_4)]$$

$$= 0.0072.$$

This error in the calculated value of the rate is enough, even at $\Delta N = 1.0$, to provide the steady state error shown in Graph 9-3. Hence, to obtain reasonable results from HIXL, the step-size in N should be small, there should be as few sweeps as possible, and the potentiometers, particularly those for y_4 and y_5 with their gains of ten, should be set as accurately as possible, especially in the first cell. This was done by placing the analog computer in the initial condition mode, forcing the values y_4, y_5 to 1.0 by temporary initial condition values on their integrators and manually setting these two potentiometers so that their output was then exactly 0.2280 and 0.1393. Once this was done, and provided the analog computer was well warmed-up, no further action was required for several runs.

The effect of this trimming was to cause $\left.\frac{d\bar{y}}{ds}\right|_1$ to tend accurately to zero at steady state. This value was continuously displayed on an oscilloscope during hybrid operation and if the final steady-state value became greater than 0.0010, then this was a sure indication of some potentiometer drift which could be corrected and the run restarted.

Inaccuracy of the second derivative $\frac{\partial^2 x}{\partial N^2}$ would affect the steady state values of $x_{N+\Delta N}$ and $x_{N+2\Delta N}$ in the same way as the rate value. However, provided the calculation of the rate was accurate and tended to zero at steady state, there was no accuracy problem with the generation of the second derivative.



POTENTIOMETER SETTING VALUES

C_1 = .2533

C_2 = .5700

C_3 = .2280

C_4 = .1393

FIGURE 9D-1. ERROR ANALYSIS OF RATE CALCULATION.

s	x	Δx	$\Delta^2 x$	S	x	Δx	$\Delta^2 x$
54	.4012			18	.3705		
		261				402	
55	.4273		-4	19	.4107		3
		257				405	
56	.4530		10	20	.4512		5
		267				410	
57	.4797		-5	21	.4922		-11
		262				399	
58	.5059		-11	22	.5321		-7
		251				392	
59	.5310		6	23	.5713		-26
		257				366	
60	.5567		-3	24	.6079		-7
		254				359	
61	.5821		-8	25	.6438		
		246					
62	.6067						
K = 1.0	ξ = 1.0	θ = 0.0	D_R = 10.0	N = 54	K = 1.2	ξ = 1.0	θ = 1.0	D_R = 10.0	N = 20

TABLE 9D-1 Finite difference table for HIXL results.

REACTION TRANSFER UNITS FROM MID-POINT SLOPE

The number of reaction transfer units is easily found from the mid-point slope

$$\left.\frac{dx}{dz}\right|_{x=0.5}$$

and Figure 3-8. However, calculation of this slope, even for computer-derived data, requires some experimentation to find a suitable method since results from HIXL contain random noise and results from BGP or VHT are widely spaced.

Finite differences for two computed breakthrough curves from HIXL have been calculated (Table 9D-1). The second differences show random noise corresponding to ± 3 to 5 × 10^{-4} in the x values.

Graph 9E-1 shows the gradient calculated for these two breakthrough curves using first and second-order differentiation formula (Hausner, 1971):-

$$\left.\frac{dx}{dS}\right|_j = \frac{x_j - x_{j-1}}{\Delta S}$$

$$\left.\frac{dx}{dS}\right|_j = \frac{x_{j+1} - x_{j-1}}{2\Delta S}$$

Random noise is eliminated (particularly for the second case) only by averaging the differentials at 3 points:-

$$\left.\frac{dx}{dS}\right|_3 = \frac{\frac{x_5 - x_3}{2\Delta S} + \frac{x_4 - x_2}{2\Delta S} \quad \frac{x_3 - x_1}{2\Delta S}}{3}$$

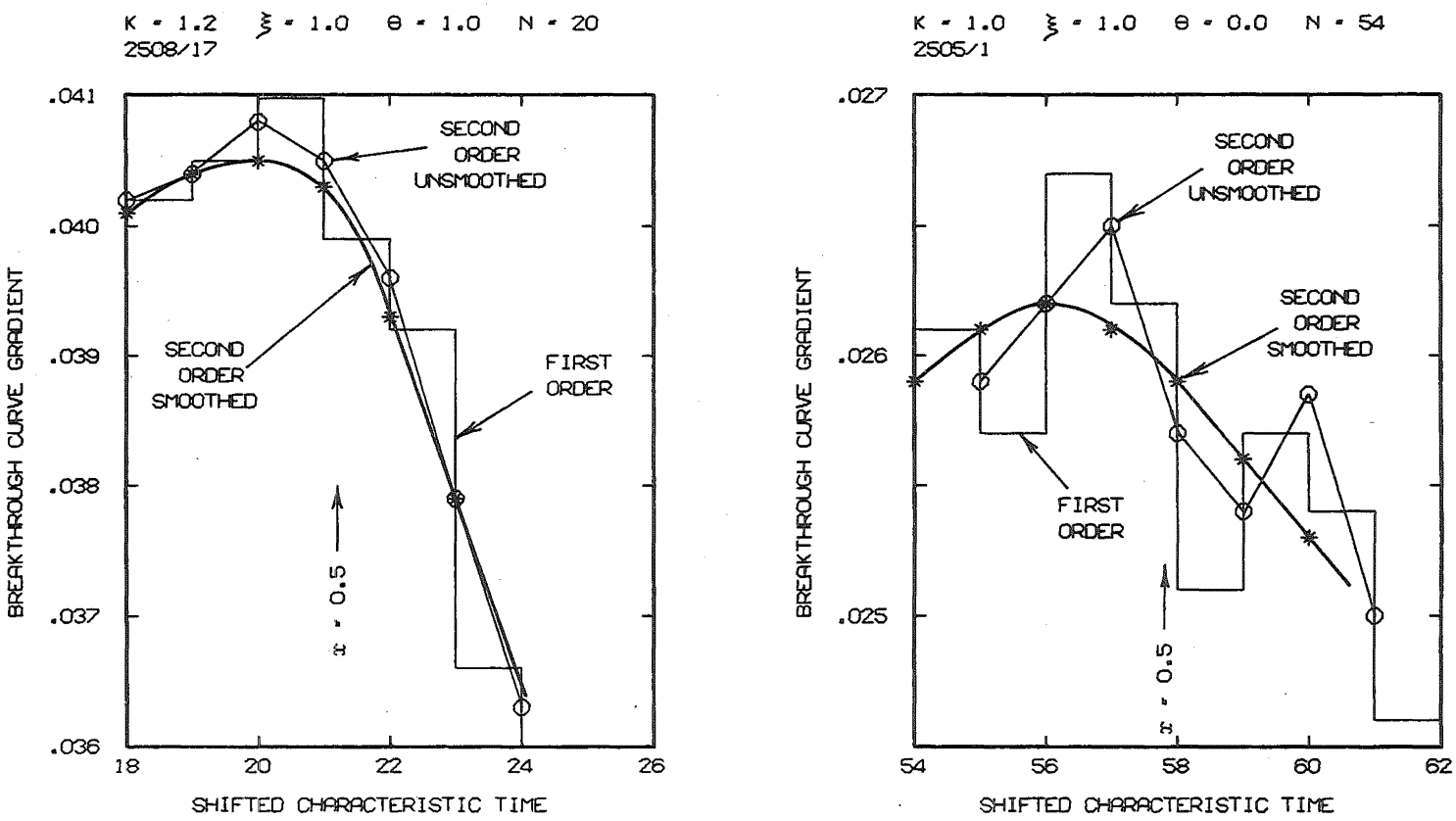
$$= \frac{x_5 + x_4 - x_2 - x_1}{6\Delta S}$$

to give the smoothed second order derivative on Graph 9D-1. This formula has been used for HIXL results, but if the data points are widely spaced, the gradient at the end points can be significantly less than that at the midpoint, resulting in an underestimate of the slope.

Results from the BGP or the VHT programs are more widely spaced but less noisy, and were numerically differentiated using a fourth-order formula (Hausner, 1971)

$$\left.\frac{dx}{dS}\right|_j = \frac{x_{j+2} - 8x_{j+1} + 8_{j-1} - x_{j-2}}{12\Delta S}$$

Since the data points are rarely available with a point exactly at $x = 0.5$, the gradient was calculated at the next point above and below this value. Graph 9E-1 shows that the linear interpolation used is adequate.



GRAPH 9E-1. DETERMINATION OF BREAKTHROUGH CURVE GRADIENTS.

CHAPTER 10

IMPLICATIONS FOR DESIGN

A number of rigorous computational models have been developed for the fixed-bed ion exchange process. This chapter is concerned with their use, firstly to establish the applicability of some of the limiting and empirical breakthrough curve expressions; secondly, to develop and assess methods of breakthrough curve prediction which are relatively unrestricted but can be used without further automatic computation; and thirdly to recommend simulation methods for design and analysis of ion exchange columns when simpler methods are not appropriate.

In general, the digital computer simulation IXLR, which has been verified in some detail and successfully compared with experimental data, has been taken as a correct representation of ion exchange column behaviour.

10-1 THE LIMITING SOLUTIONS

The two limiting assumptions which have been used to derive analytical breakthrough curve equations are:-

(a) Proportionate pattern (Section 3-1) for unfavourable equilibrium with no rate limitations

(b) Constant pattern (Section 3-3) for favourable equilibrium and a range of mass transfer rate possible mass transfer rate mechanisms.

Both methods are restricted to a constant separation factor and the standard initial and boundary conditions (i.e. initially solute-free column and constant feed solution concentration).

10-1-1 Proportionate Pattern

Graphs 10-1 to 10-3 compare proportional pattern breakthrough curves (Eqn 3- 7):-

$$x = \frac{1 - \sqrt{\frac{K}{Z}}}{1 - K} \qquad (10\text{-}1)$$

with the results of IXLR, for separation factors of 0.8, 0.5 and 0.1 with 20, 50 and 100 transfer units.

The proportionate pattern equation assumes that equilibrium is so unfavourable that rate effects are irrelevant and consequently the bulk phases are in equilibrium. Breakthrough curves are then dependent only on equilibrium (K) and throughput (Z).

The graphs (which have been plotted against T to show the effect of N) indicate that the equilibrium has to be very unfavourable (K approaching 0.1) before the proportionate pattern equation is a good fit to the computed curves, especially for low x. Application in this range is limited because regeneration of an industrial column with such unfavourable equilibrium would be so difficult as to make the separation by ion exchange uneconomical. In addition, the proportionate pattern solution fails to follow the effect of the mechanism parameter, and the mid-point slope is too steep.

Some case should be made for this equation by its simplicity. Its range can be extended (perhaps to K = 0.5 with moderate accuracy) by arbitrarily correcting by eye its defects in comparison with Graphs 10-1 to 10-3.

10-1-2 Constant Pattern

The equations for the constant pattern solutions are (Table 3-3):-

Particle control $$T - N = \frac{1}{K - 1} \ln(x) - \frac{K}{K - 1} \ln(1 - x) - 1 \qquad (10\text{-}2)$$

Solution control $$T - N = \frac{K}{K - 1} \ln(x) - \frac{1}{K - 1} \ln(1 - x) + 1 \qquad (10\text{-}3)$$

Reaction kinetics $$T_R - N_R = \frac{K}{K - 1} \ln\left(\frac{x}{1 - x}\right) \qquad (10\text{-}4)$$

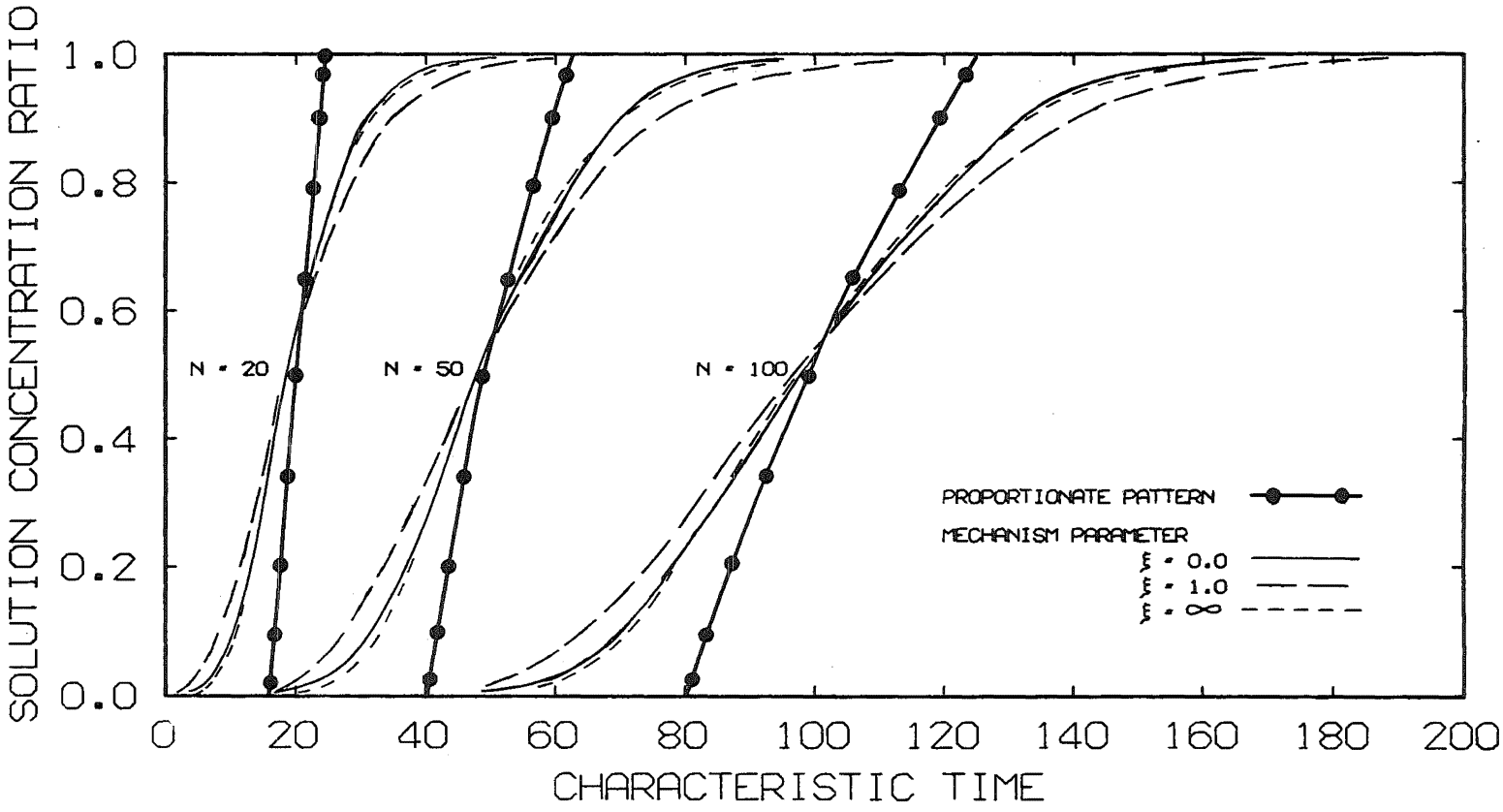
where N is the number of transfer units

T the characteristic time

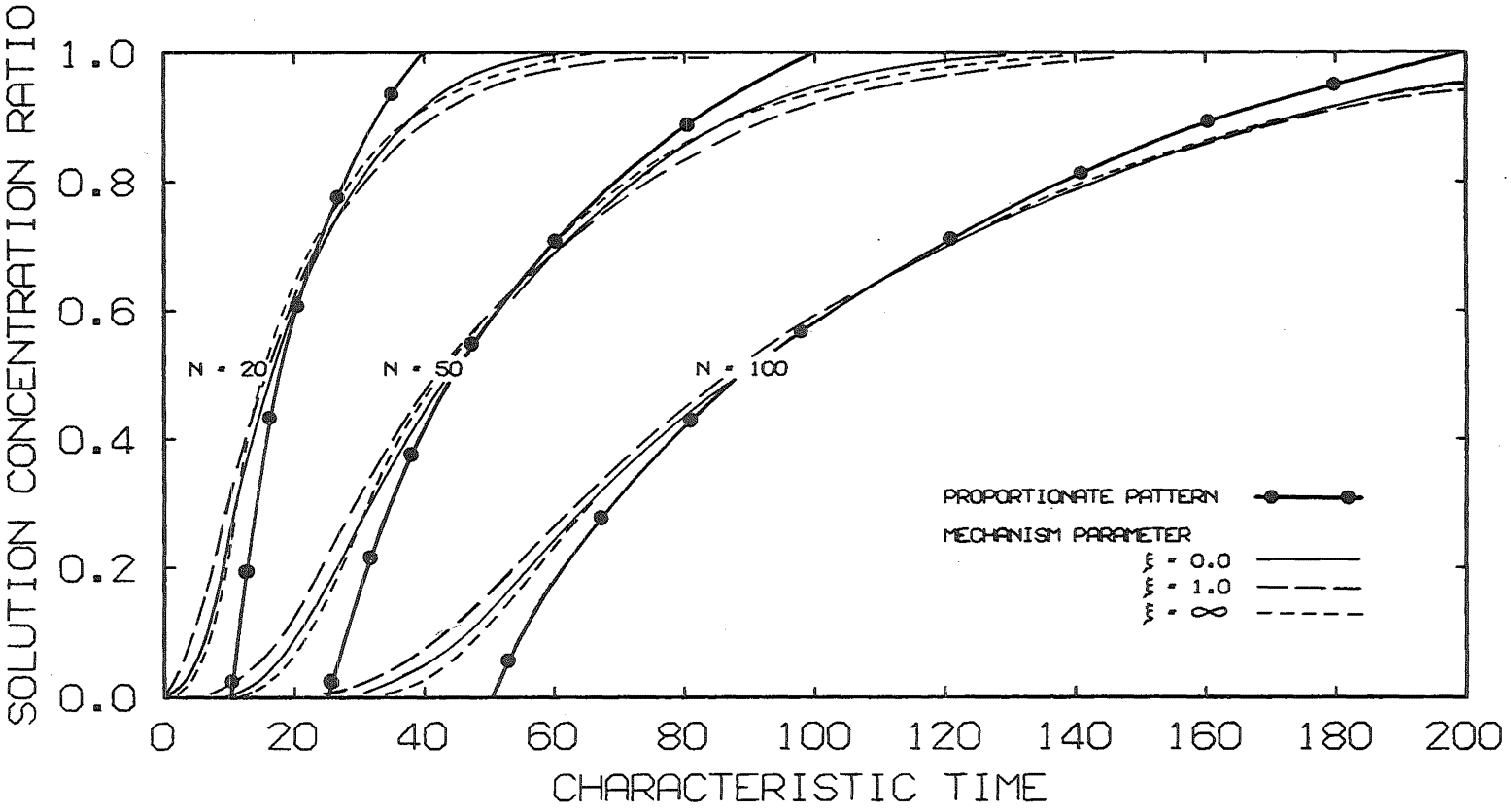
N_R, T_R the number of transfer units and the characteristic time, reaction kinetic basis.

These equations satisfy the constant pattern requirement that T - N is independent of N.

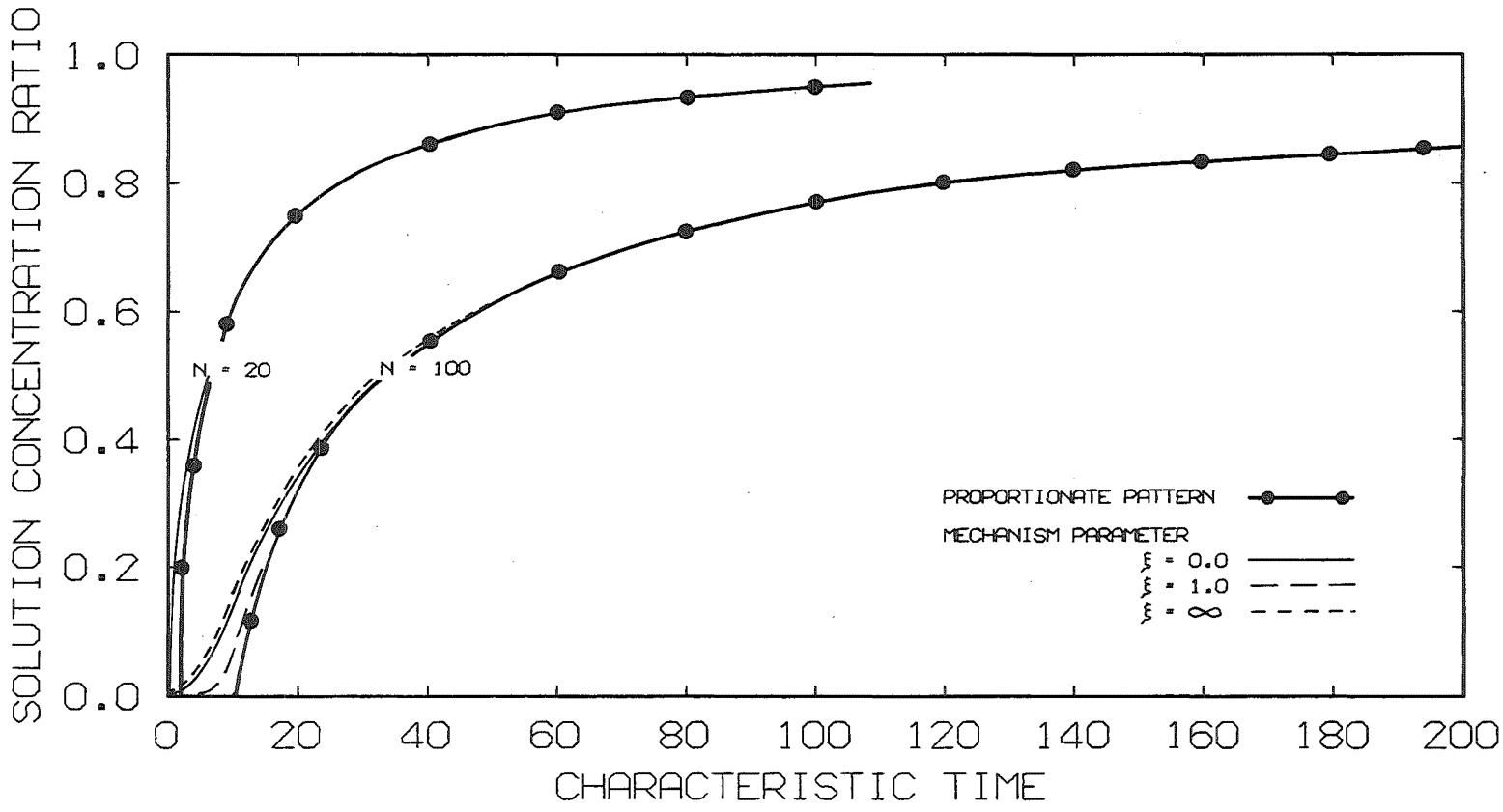
Values from the tabulation of general breakthrough curves (GBC) in Appendix 5E, computed using IXLR, asymptotically approach results calculated from Eqns 10-2, 10-3 as the numbers of transfer units increase (Tables 10-1, 10-2). For K = 1.2, constant pattern conditions



GRAPH 10-1. COMPUTED RESULTS AND THE PROPORTIONATE PATTERN SOLUTION
K = 0.8



GRAPH 10-2. COMPUTED RESULTS AND THE PROPORTIONATE PATTERN SOLUTION
K = 0.5



GRAPH 10-3. COMPUTED RESULTS AND THE PROPORTIONATE PATTERN SOLUTION
K = 0.1

have still not been attained at 200 transfer units. However, the good agreement at more favourable equilibrium is a further verification of IXLR.

The derivations of both Eqn 10-2 and the model IXLR use the linear particle rate expression (Eqn 2-27b). Hall et al. (1966) have developed a digital computer solution for the constant pattern condition which allows for fickian diffusion within the resin particle. Graph 10-4 compares their computed results with those from GBC, for particle control and K = 1.2, 2.0, 10.0. The small difference can be attributed to the different expressions used for the particle rate. This graph corresponds to the very conditions where the difference due to the particle rate expressions would be greatest (i.e. favourable equilibrium and particle control) and the agreement is sufficiently good to support the conclusion of Chapter 7 that the models IXLR and IXM (which differ in the same way) produce equivalent results.

Constant pattern conditions occur for other than complete film or particle control, as inspection of the GBC values in Appendix 5E will show. There is no equation of the type of Eqn 10-1 or 10-2 for distributed mass transfer resistance, but the empirical reaction kinetic constant pattern solution gives results for all values of the mechanism parameter, through the correlation of the correction factor, b. Table 10-3 compares this equation with Eqns 10-1 and 10-2 for complete particle or film control with separation factor values of 1.2, 2.0 and 10.0. The reaction-kinetic solution provides good agreement, with its predictions lying between those for film and particle control (or those for the equivalent GBC solution).

Table 10-4 continues the examination of the reaction-kinetic method for ξ = 1.0 in comparison with GBC values. The agreement is of a similar order to Table 10-3, at least until very favourable equilibrium values are reached (K = 10.0, rather large for industrial ion exchange columns) where the reaction-kinetic predictions are significantly steeper than those for GBC.

Graph 10-5 is a summary of these tables. Eqns 10-2 to 10-4 agree with GBC for constant pattern conditions with the exception

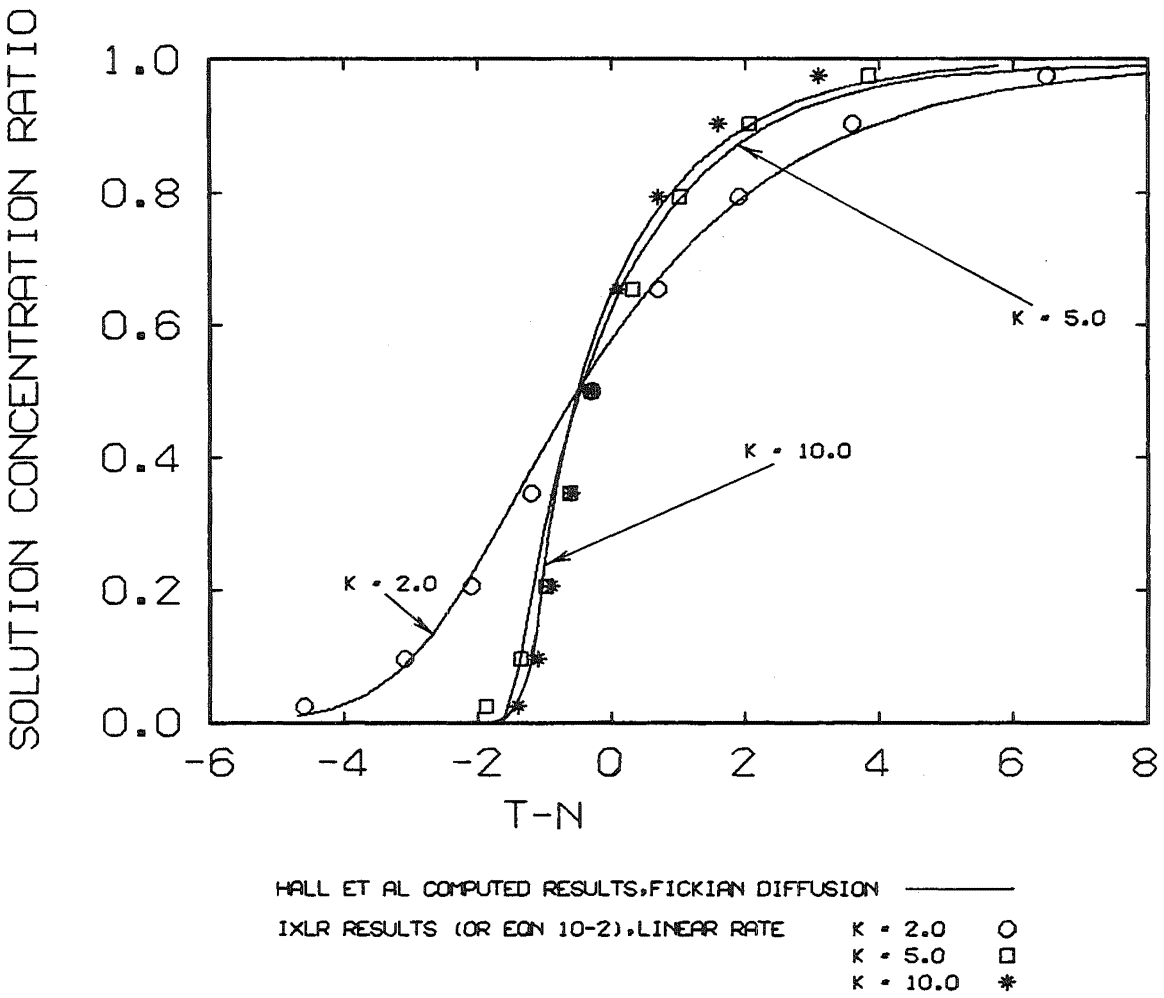
	T − N values										
	IXLR				Constant Pattern	IXLR			Constant Pattern	IXLR		Constant Pattern
x	N=80	120	160	200	Eqn 10-2	N=10	20	30	Eqn 10-2	N=10	20	Eqn 10-2
.0245	-15.1	-16.7	-17.6	-18.2	-19.4	-4.1	-4.5	-4.6	-4.7	-1.5	-1.5	-1.4
.0955	- 9.8	-10.7	-11.2	-11.6	-12.1	-2.9	-3.1	-3.1	-3.2	-1.2	-1.3	-1.2
.2061	- 6.2	-6.7	-7.0	-7.2	- 7.5	-1.9	-2.1	-2.1	-2.1	-0.9	-0.9	-0.9
.3455	- 3.2	-3.4	-3.5	-3.6	- 3.8	-1.1	-1.2	-1.2	-1.2	-0.7	-0.7	-0.7
.5000	- 0.3	-0.3	-0.3	-0.3	- 0.3	-0.3	-0.3	-0.3	-0.3	-0.3	-0.3	-0.3
.6545	2.7	2.9	3.1	3.1	3.3	0.6	0.7	0.7	0.7	0.1	0.1	0.1
.7939	6.0	6.5	6.8	7.0	7.3	1.8	1.9	1.9	1.9	0.7	0.7	0.7
.9045	10.3	11.1	11.7	12.0	12.6	3.3	3.5	3.6	3.6	1.6	1.6	1.6
.9755	16.9	18.5	19.4	19.9	21.3	5.9	6.3	6.4	6.4	3.1	3.1	3.1
	K=1.2		ξ= 0.0				K=2.0		ξ=0.0		K=10.0	ξ=0.0

TABLE 10-1. A comparison of IXLR results with the analytical solution for constant pattern conditions and particle phase control.

T-N values

x	IXLR N=80	120	160	200	Constant Pattern Eqn 10-3	IXLR N=10	20	30	Constant Pattern Eqn 10-3	IXLR N=10	20	Constant Pattern Eqn 10-3
.0245	-16.3	-17.9	-19.1	-19.7	-21.1	-5.4	-6.1	-6.3	-6.4	-3.1	-3.2	-3.1
.0955	-10.2	-11.1	-11.6	-12.0	-12.6	-3.3	-3.5	-3.6	-3.6	-1.6	-1.7	-1.6
.2061	- 6.1	- 6.6	- 6.9	- 7.0	- 7.3	-1.9	-1.9	-1.9	-1.9	-0.7	-0.8	-0.7
.3455	- 2.8	- 3.0	- 3.1	- 3.2	- 3.3	-0.7	-0.7	-0.7	-0.7	-0.1	-0.2	-0.1
.5000	0.1	0.2	0.2	0.2	0.3	0.2	0.3	0.3	0.3	0.3	0.3	0.3
.6545	3.0	3.3	3.5	3.6	3.8	1.1	1.2	1.2	1.2	0.6	0.6	0.6
.7939	6.1	6.7	7.0	7.2	7.5	1.9	2.1	2.1	2.1	0.9	0.8	0.9
.9045	9.9	10.8	11.3	11.6	12.1	2.9	3.1	3.1	3.2	1.2	1.2	1.2
.9755	15.8	17.1	17.9	18.5	19.4	4.4	4.7	4.7	4.7	1.4	1.4	1.4
	K=1.2			$\xi=\infty$		K =2.0		$\xi=\infty$		K=10.0		$\xi=\infty$

TABLE 10-2. A comparison of IXLR results with the analytical solution for constant pattern conditions and film control.



GRAPH 10-4. CONSTANT PATTERN BREAKTHROUGH CURVES FOR PARTICLE CONTROL FOR LINEAR AND FICKIAN PARTICLE DIFFUSION MODELS.

noted above for very favourable equilibrium. However, the reaction kinetic method provides useful predictions for constant pattern operation over the range corresponding to current ion exchange practice. The ability to include the effect of the mechanism parameter indicates that this equation should be used rather than the particle or film control expressions. The same conclusion has been previously reached (Kelly, Allen and Kennedy, 1970) based on experimental results.

Before the performance of any ion exchange column can be expressed in terms of a constant pattern assumption, preliminary information must be available on the approach to the asymptotic solution as the number of transfer units in the column is increased. If the number of transfer units is insufficient for constant pattern conditions, then the asymptotic expression should not be used. Hiester et al. (1963, Table 16-19) have provided guidance in the form of a relation between N_{min} (the minimum number of transfer units for constant pattern) and the separation factor (Table 3-4 or Graph 10-6). These recommendations were made on the basis of the reaction-kinetic solution and the attainment of constant pattern was defined when all solution concentration values were within 0.01 of the asymptotic solution.

Using the IXLR model, these recommendations have been substantially confirmed (Graph 10-6). Constant pattern conditions are defined on the basis that the root-mean-square deviation in (T - N) from the limiting value is less than 1% of the width of the breakthrough curve from $x = 0.0245$ to 0.9755. This graph defines the region for which constant pattern conditions can be assumed and the limiting equations used. Equally, the GBC results themselves can be used to provide breakthrough curves, with the constant pattern condition used to make interpolation easier.

10-2 THE REACTION-KINETIC (VHT) SOLUTION

The reaction-kinetic method for describing ion exchange breakthrough curves (Section 3-4) has been used in Chapter 9 to correlate the results of the hybrid computer model HIXL with axial dispersion. This section further supports the general use of the reaction-kinetic expression by showing that it gives results that are essentially the

T - N values

x	K = 1.2 Particle	K = 1.2 Film	K = 1.2 Reaction Kinetics	K = 2.0 Particle	K = 2.0 Film	K = 2.0 Reaction Kinetics	K = 10.0 Particle	K = 10.0 Film	K = 10.0 Reaction Kinetics
.0245	-19.4	-21.1	-20.3	-4.7	-6.4	-5.8	-1.4	-3.1	-2.2
.0955	-12.1	-12.6	-12.4	-3.2	-3.6	-3.4	-1.2	-1.6	-1.4
.2061	- 7.5	- 7.3	- 7.4	-2.1	-1.9	-2.0	-0.9	-0.7	-0.8
.3455	- 3.8	- 3.3	- 3.5	-1.2	-0.7	-1.0	-0.7	-0.1	-0.4
.5000	- 0.3	0.3	0.0	-0.3	0.3	0.0	-0.3	0.3	0.0
.6545	3.3	3.8	3.5	0.7	1.2	1.0	0.1	0.6	0.4
.7939	7.3	7.5	7.4	1.9	2.1	2.0	0.7	0.9	0.8
.9045	12.6	12.1	12.4	3.6	3.2	3.4	1.6	1.2	1.4
.9755	21.1	19.4	20.3	6.4	4.7	5.8	3.1	1.4	2.2
b			1.09			1.33			1.82

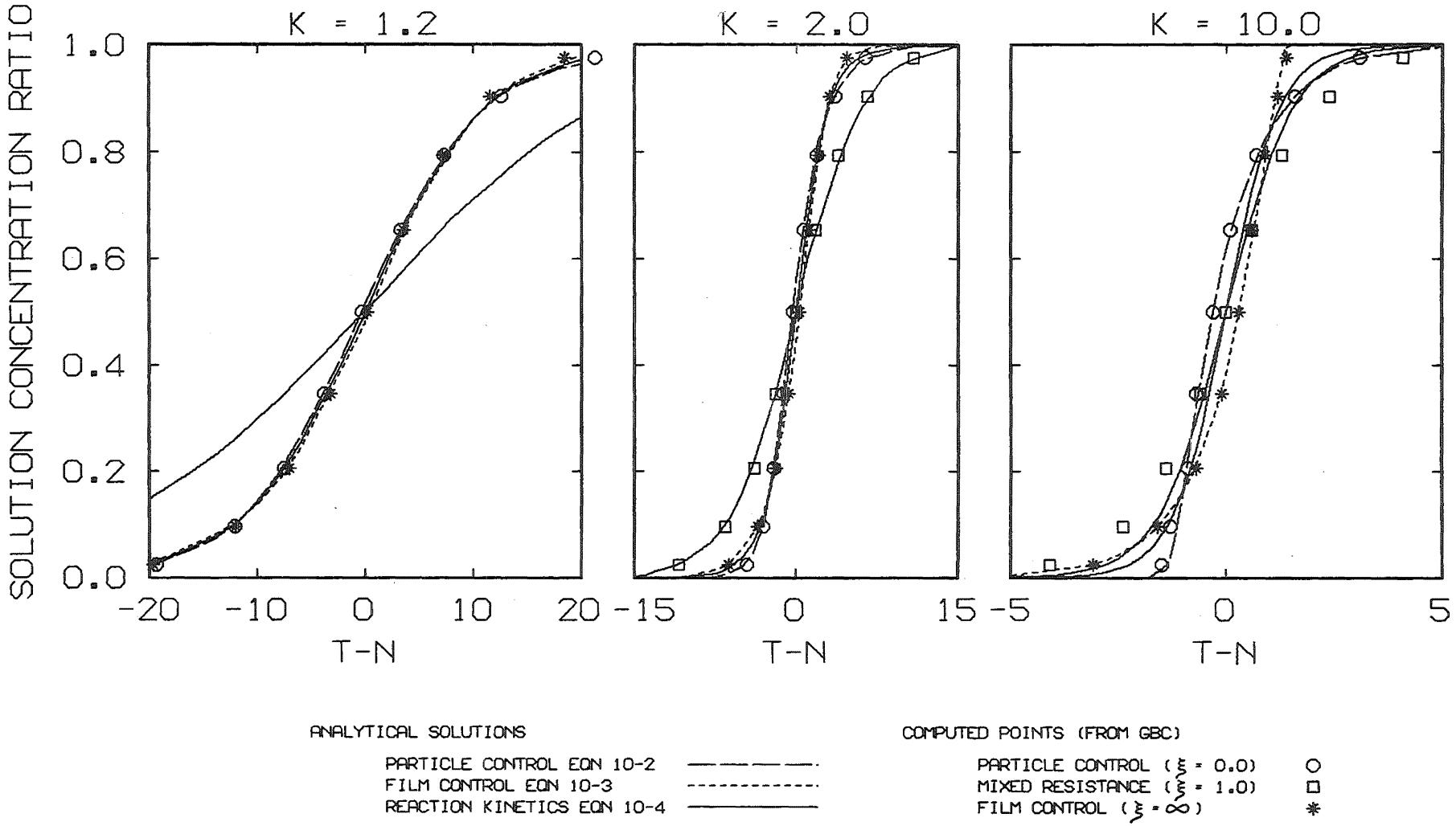
For the reaction kinetic values $T - N = \frac{T_R - N_R}{b}$

TABLE 10-3. A comparison of the analytical reaction kinetic predictions (Eqn 10-4) for constant pattern conditions with those for film and particle control (Eqns 10-2, 10-3).

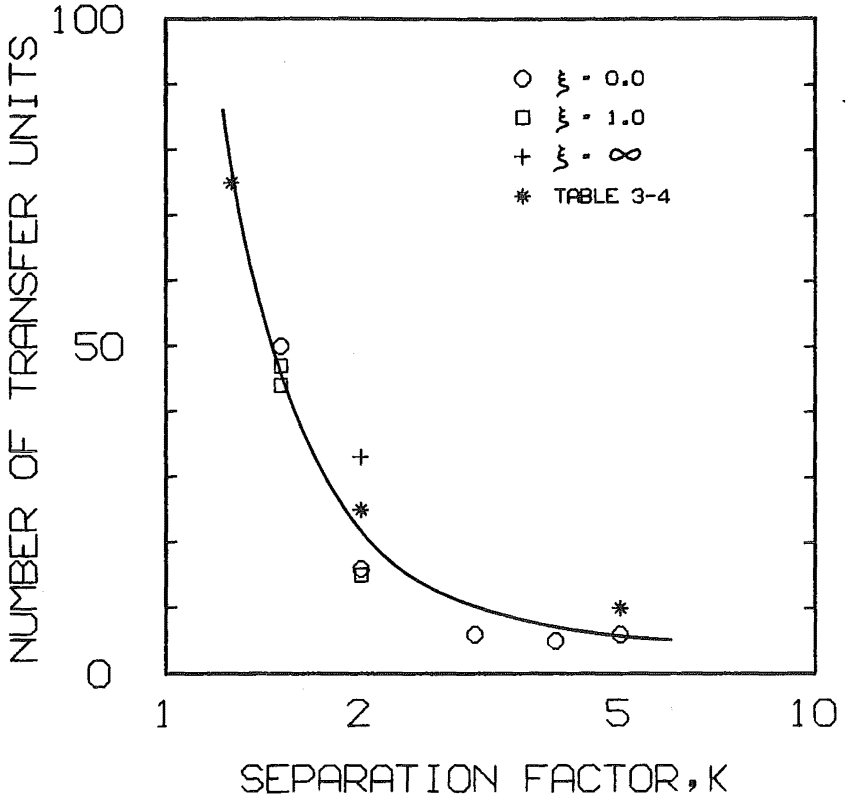
T - N values

x	K = 1.2		K = 2.0		K = 4.0		K = 10.0	
	Reaction Kinetics	IXLR	Reaction Kinetics	IXLR	Reaction Kinetics	IXLR	Reaction Kinetics	IXLR
.0245	-40.6	-	-11.6	-10.9	-6.1	-5.8	-2.8	-4.1
.0955	-24.8	-	- 6.8	- 6.6	-3.8	-3.5	-1.7	-2.4
.2061	-14.9	-	- 4.1	- 3.9	-2.3	-2.1	-1.0	-1.4
.3455	- 7.0	Constant	- 2.0	- 1.9	-1.1	-1.0	-0.5	-0.6
.5000	0.0	pattern	0.0	0.0	0.0	0.0	0.0	0.0
.6545	7.0	not	2.0	1.8	1.1	1.0	0.5	0.6
.7939	14.9	attained	4.1	3.9	2.3	2.1	1.0	1.3
.9045	24.8	-	6.8	6.6	3.8	3.5	1.7	2.4
.9755	40.6	-	11.1	10.9	6.1	5.9	2.8	4.1
b	1.09		1.33		1.60		2.9	

TABLE 10-4 A comparison of IXLR results with the analytical reaction kinetic solution for constant pattern conditions, and distributed mass transfer resistance.



GRAPH 10-5. COMPARISON OF CONSTANT PATTERN ANALYTICAL SOLUTIONS WITH COMPUTED RESULTS.



GRAPH 10-6. THE ATTAINMENT OF CONSTANT PATTERN CONDITIONS.

same as those of IXLR as generalised in the GBC tabulation.

For linear equilibrium, the reaction-kinetic solution and the model IXLR solve exactly the same equations, and their results should be the same. Graph 10-7 and 10-8 show that this is the case both for total film or particle mass transfer resistance and for equally-distributed resistance.

For non-linear equilibrium, the reaction-kinetic solution remains an equally good expression of the IXLR model results (Graph 10-9, 10-10), as do the final four plots (Graphs 10-11 to 10-14) which are at the extremes of the region investigated:-

Separation factor	Mechanism parameter
0.1	0.0
10.0	0.0
0.1	∞
10.0	∞

The reaction-kinetic model, which was based on an empirical rate expression but which has an analytical solution, has produced results which are very close to those produced by the digital computer solution of the more rigorous IXLR model.

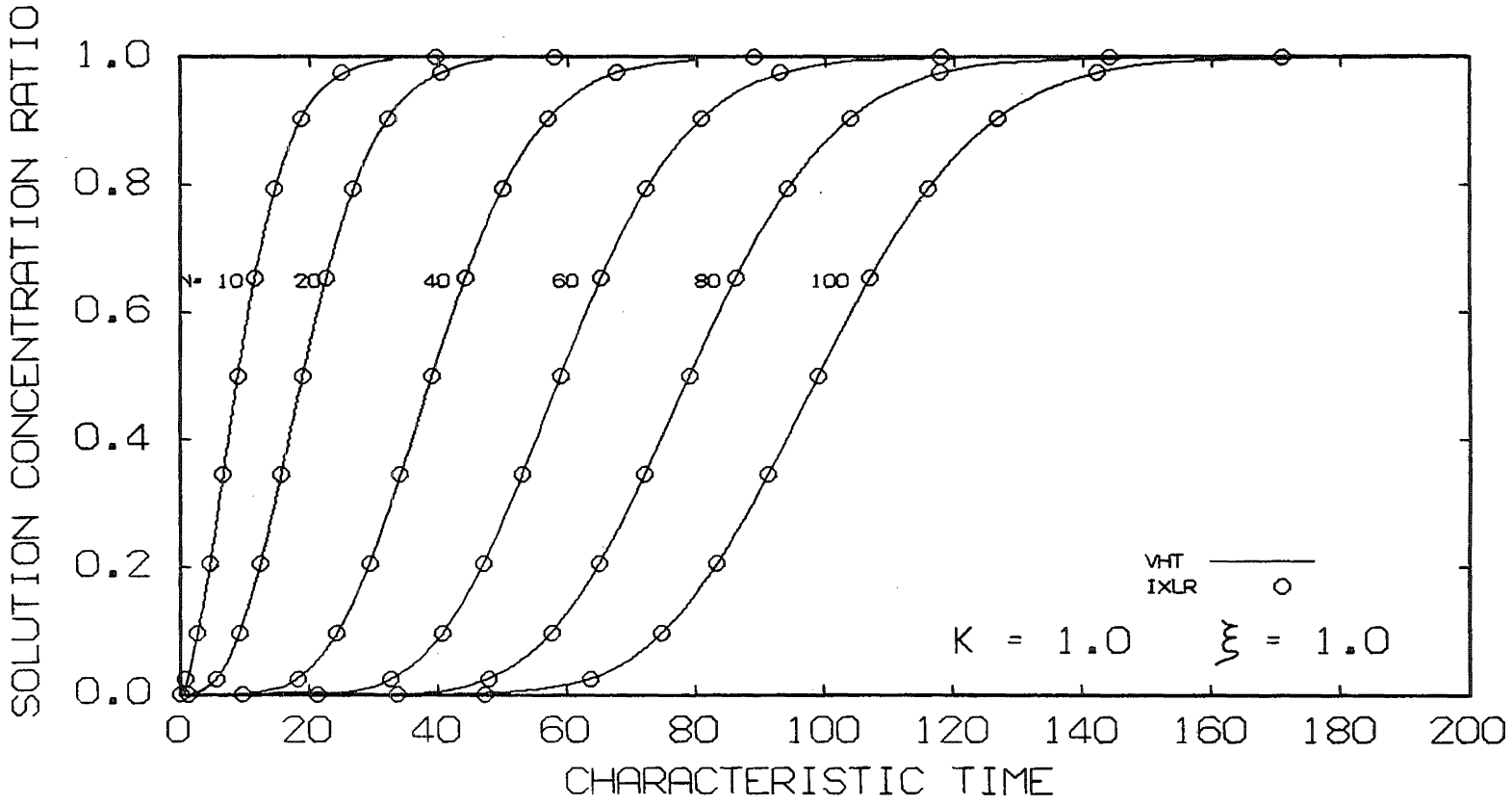
10-3 SHORT-CUT METHODS

One of the aims of this thesis was to develop short-cut methods of calculating fixed-bed ion exchange breakthrough curves that would be reasonably accurate and which could be used with a minimum of calculational effort, rather like the short-cut methods of distillation column design (Van Winkle, 1967).

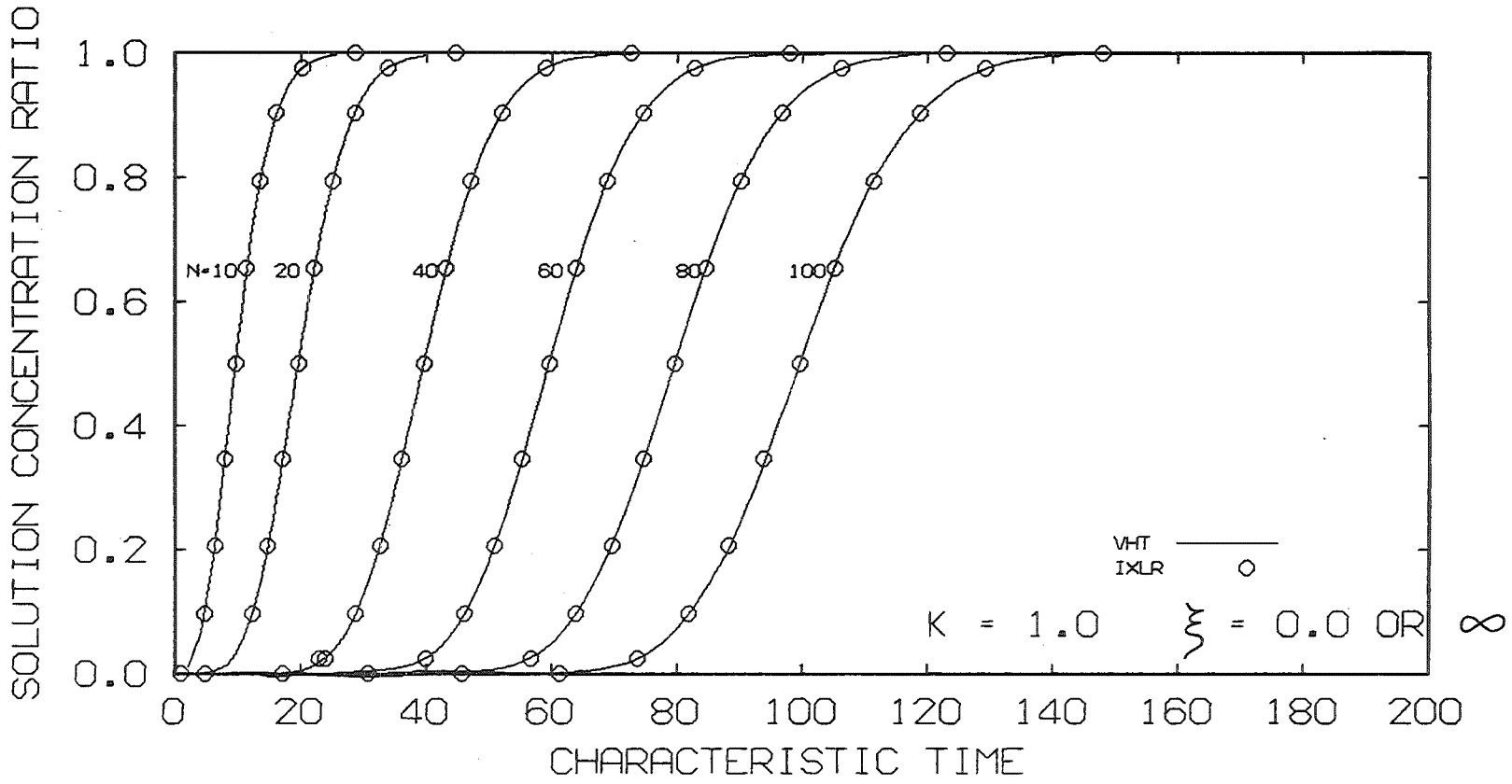
Several empirical methods were used to correlate the information contained in the GBC tabulation. The most successful of these was based on the remarkable linearisation of breakthrough curves with the Weibull distribution function (Steiger, 1971) in the form:-

$$x = 1 - \exp\left[\left(\frac{T - \gamma}{\alpha}\right)^{\beta}\right] \qquad (10\text{-}5)$$

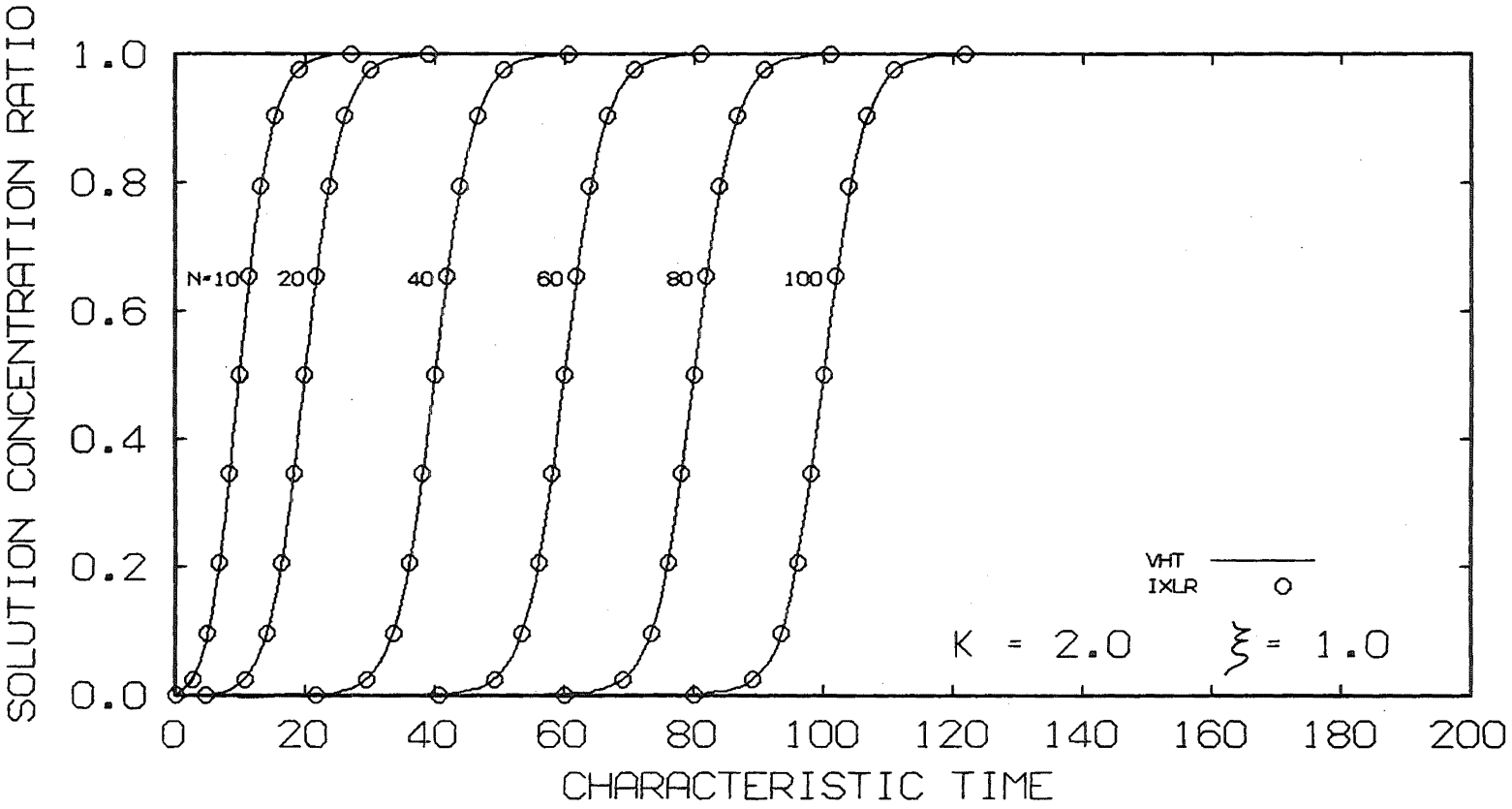
where α, β and γ are constants. With suitable transformation:-



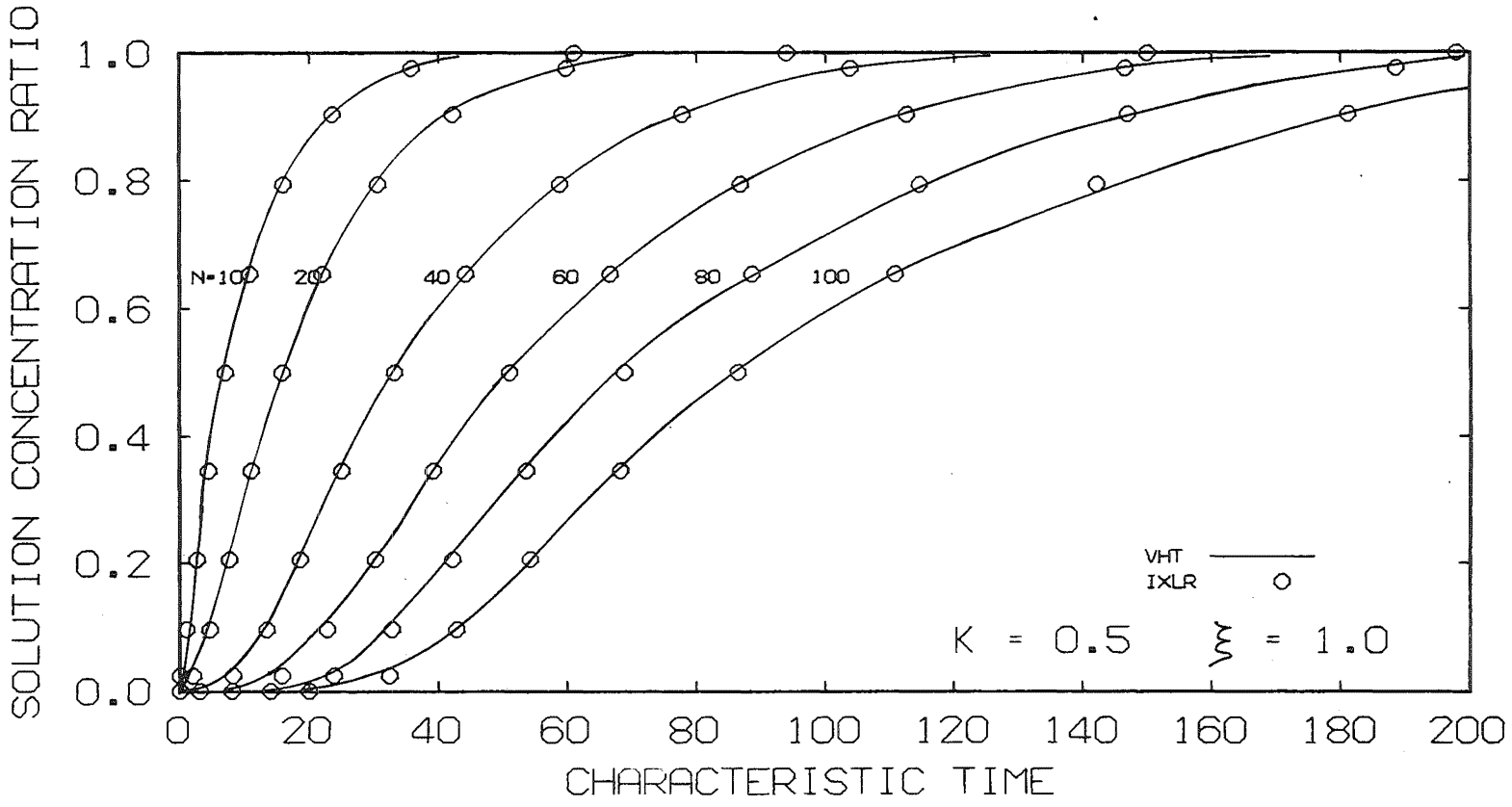
GRAPH 10-7. COMPARISON OF THE REACTION KINETIC SOLUTION WITH COMPUTED RESULTS.



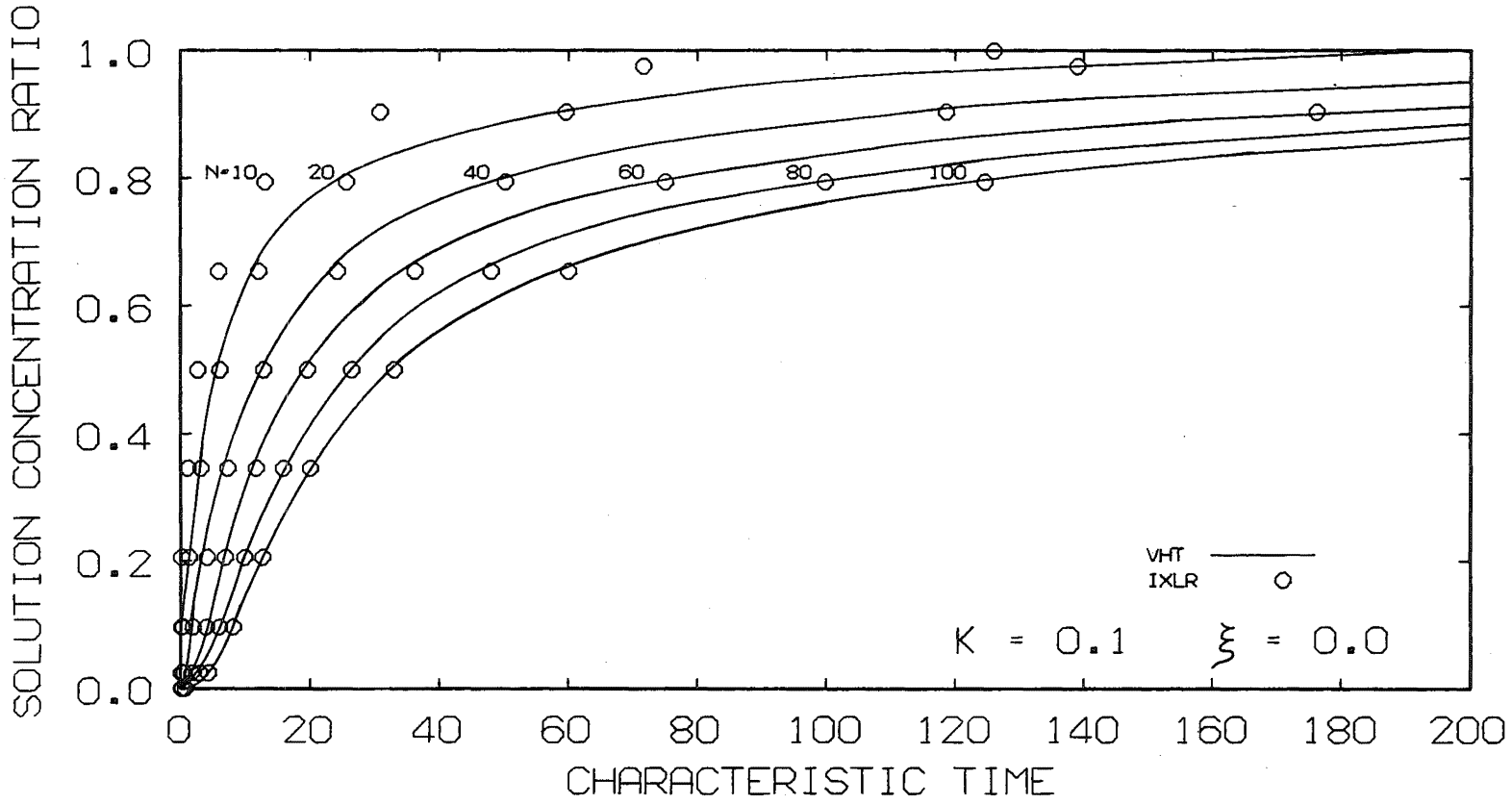
GRAPH 10-8. COMPARISON OF THE REACTION KINETIC SOLUTION WITH COMPUTED RESULTS.



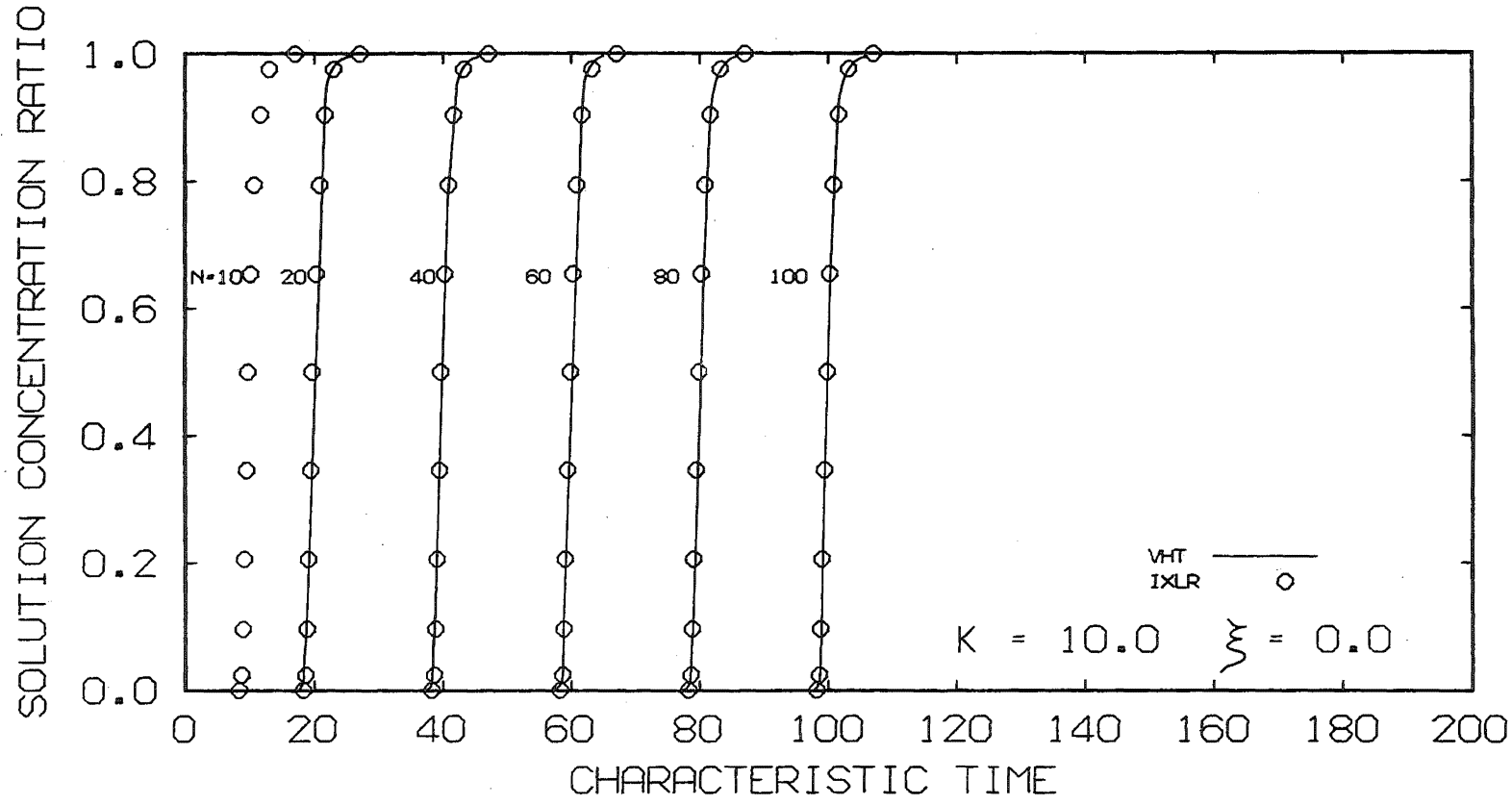
GRAPH 10-9. COMPARISON OF THE REACTION KINETIC SOLUTION WITH COMPUTED RESULTS.



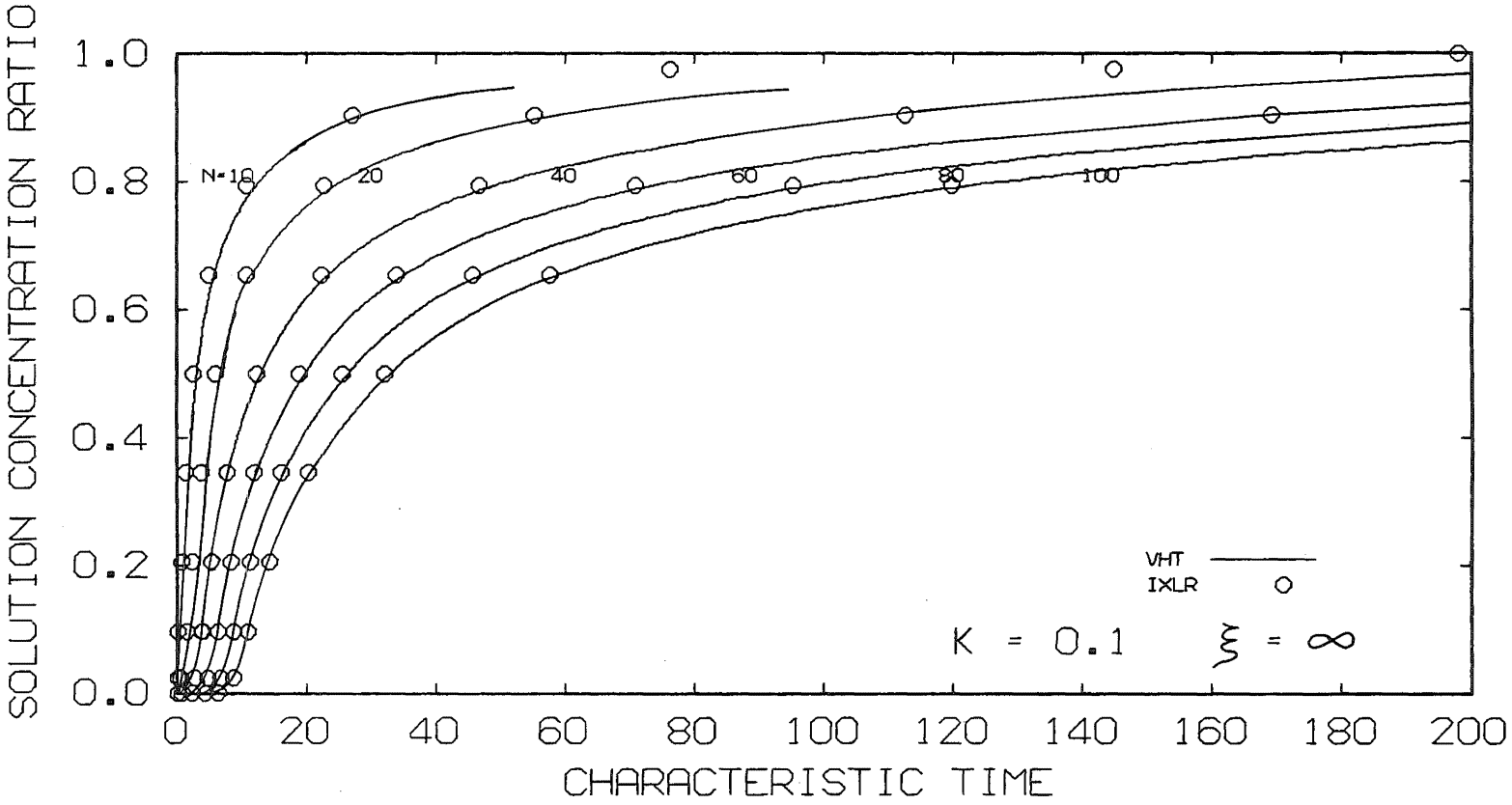
GRAPH 10-10. COMPARISON OF THE REACTION KINETIC SOLUTION WITH COMPUTED RESULTS.



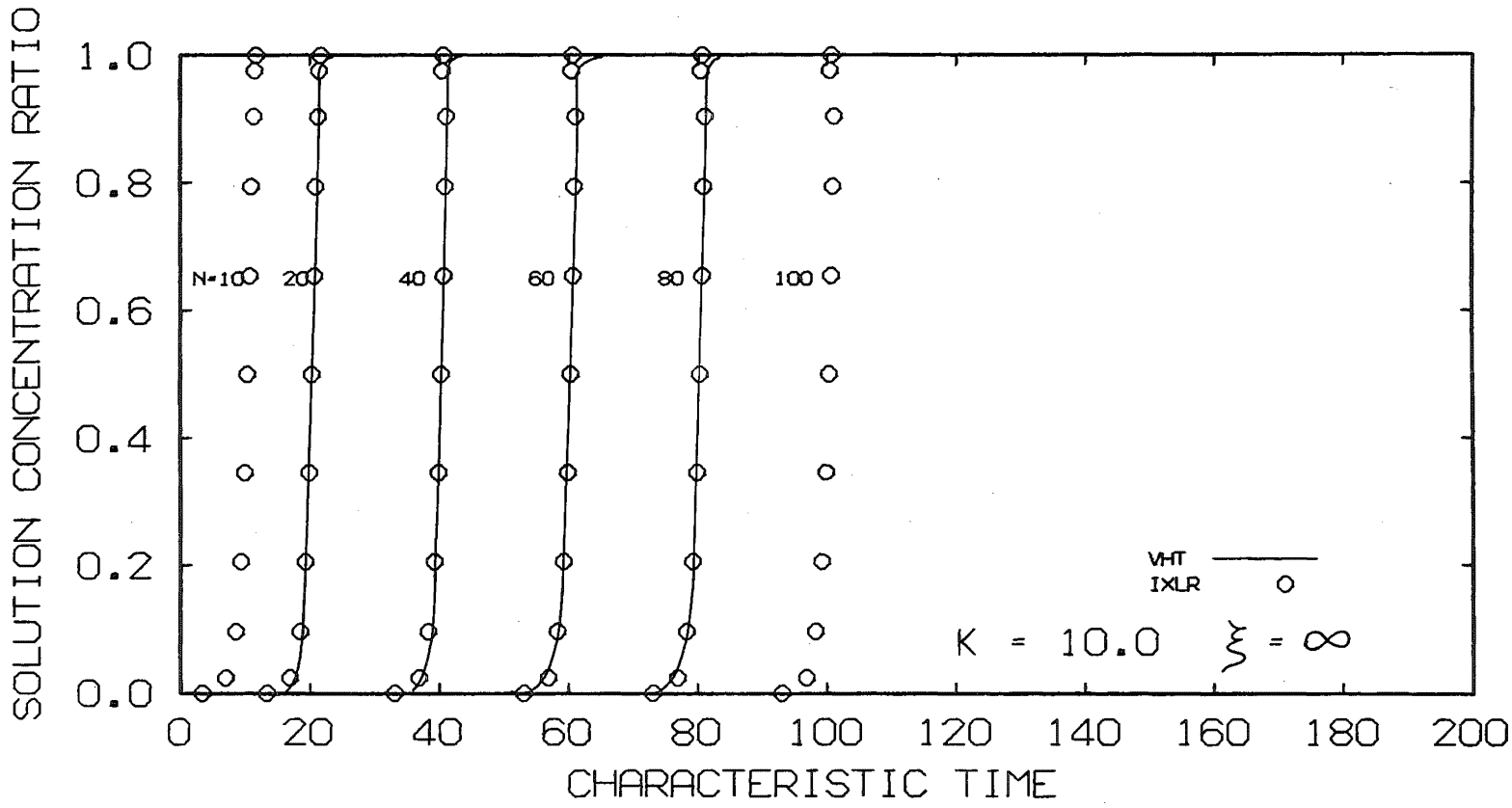
GRAPH 10-11. COMPARISON OF THE REACTION KINETIC SOLUTION WITH COMPUTED RESULTS.



GRAPH 10-12. COMPARISON OF THE REACTION KINETIC SOLUTION WITH COMPUTED RESULTS.



GRAPH 10-13. COMPARISON OF THE REACTION KINETIC SOLUTION WITH COMPUTED RESULTS.



GRAPH 10-14. COMPARISON OF THE REACTION KINETIC SOLUTION WITH COMPUTED RESULTS.

$$\ln \ln \left(\frac{1}{1-x}\right) = \beta \ln(T - \gamma) - \beta \ln \alpha \qquad (10\text{-}6)$$

Graph paper is available on which ion exchange breakthrough curves are almost a straight line (Graph 10-15). The expression reduces to two parameters (as does the reaction-kinetic form), since the quantity $\frac{\alpha}{N} + \frac{\gamma}{N}$ remains reasonably constant over all the results in GBC at 1.07. The parameters α, β have been correlated against K and ξ, but the accuracy of the method is inferior to the reaction kinetic solution and has not been proceeded with.

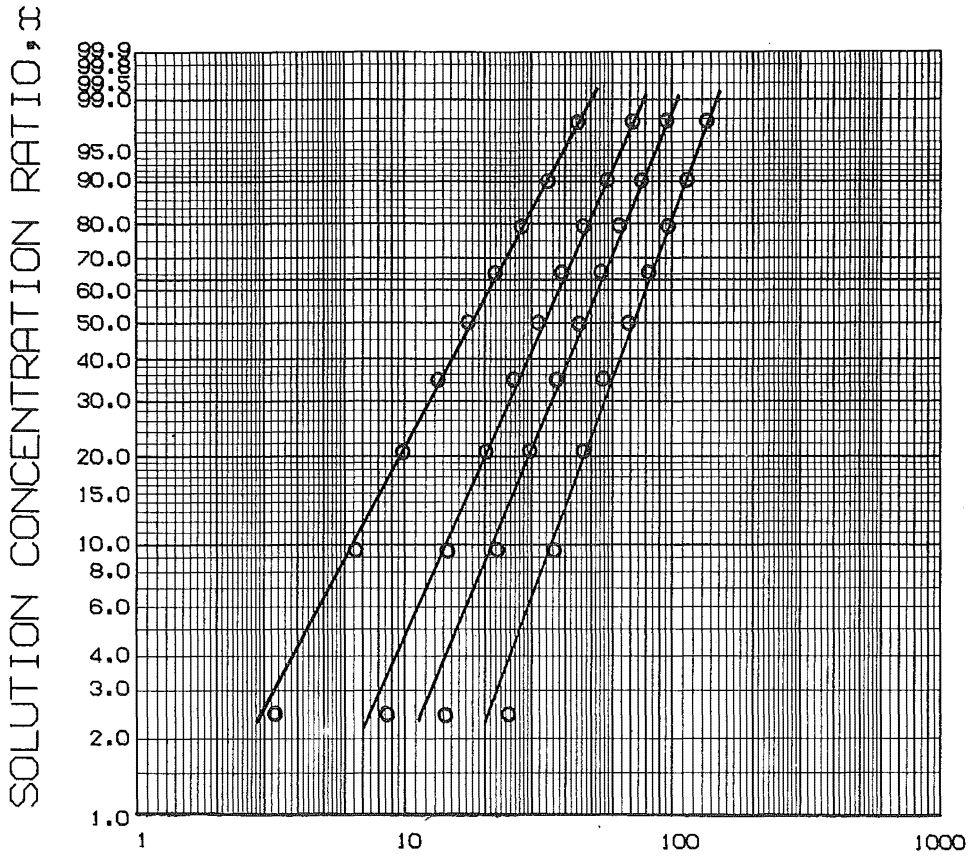
The BGC tabulation itself can be used with appropriate interpolation to draw a required breakthrough curve. However, some values, particularly in the separation factor, are too widely spaced for this purpose.

The reaction-kinetic method satisfies the requirement for a short cut method for predicting complete breakthrough curves. It is accurate and relatively easy to use, either from a tabulation of the J function (Eqn 3-23):-

$$x = \frac{K\left(\frac{N_R}{K},\ T_R\right)}{J\left(\frac{N_R}{K},\ T_R\right) + \left[1 - J\left(N_R,\ \frac{T_R}{K}\right)\right] \cdot \exp\left[-\frac{(K-1)}{K}(T_R - N_R)\right]}$$

or the error function (Hiester and Vermeulen, 1952)

$$\frac{1}{x} = 1 + \frac{\sqrt{\pi}\left\{1 - \operatorname{erf}\left[\sqrt{\frac{T_R}{K}} - \sqrt{N_R}\right]\right\} \cdot \exp\left[\left(\sqrt{\frac{T_R}{K}} - \sqrt{N_R}\right)^2\right] - \frac{1}{\sqrt{\frac{T_R}{K}} + \sqrt[4]{\frac{N_R T_R}{K}}}}{\sqrt{\pi}\left\{1 - \operatorname{erf}\left[\sqrt{\frac{N_R}{K}} - \sqrt{T_R}\right]\right\} \cdot \exp\left[\left(\sqrt{\frac{N_R}{K}} - \sqrt{T_R}\right)^2\right] + \frac{1}{\sqrt{T_R} + \sqrt[4]{\frac{N_R T_R}{K}}}}$$



$K = 0.5 \quad \xi = 1.0 \quad N = 20, 40, 60, 100$

GRAPH 10-15. BREAKTHROUGH CURVE BEHAVIOUR EXPRESSED IN TERMS OF THE WEIBULL DISTRIBUTION FUNCTION.

which should be used when $\sqrt{\frac{N_R T_R}{K}}$ is more than 6 to evade the numerical difficulties of evaluating Eqn 3-23. In this basic form, the reaction-kinetic solution includes non-linear equilibrium and distributed mass-transfer resistance for complete exhaustion or regeneration. However, the method can be extended with correction for axial dispersion (Section 9-9) or with arbitrary initial and boundary conditions (Appendix 3D). This latter modification can be compared with other less rigorous proposals (Pancharatram, Klein and Vermeulen, 1969; Dodds and Tondeur, 1972) for cyclic operation.

For column design or analysis if complete breakthrough curves are required, there is little need for computer methods other than to evaluate the reaction-kinetic equations, which is almost within the capability of a programmable calculator. The reaction-kinetic method can be used for partial breakthrough curves or cyclic operation if the modifications of Appendix 3D are incorporated. The simple integrals can be evaluated by hand or by a computer method.

The reaction-kinetic method cannot be modified to some effect just outside its assumptions. In particular, as Section 5-6-2 has shown, breakthrough curve shape will be significantly altered if the separation factor is concentration dependent. A general subroutine, called SIXFBC, is included in Appendix 10A which is derived from IXLR and its modification to include a variable separation factor, and intended for use with non-standard initial and boundary conditions. Graph 10-16 presents results from this program for the following ion exchange cycles:-

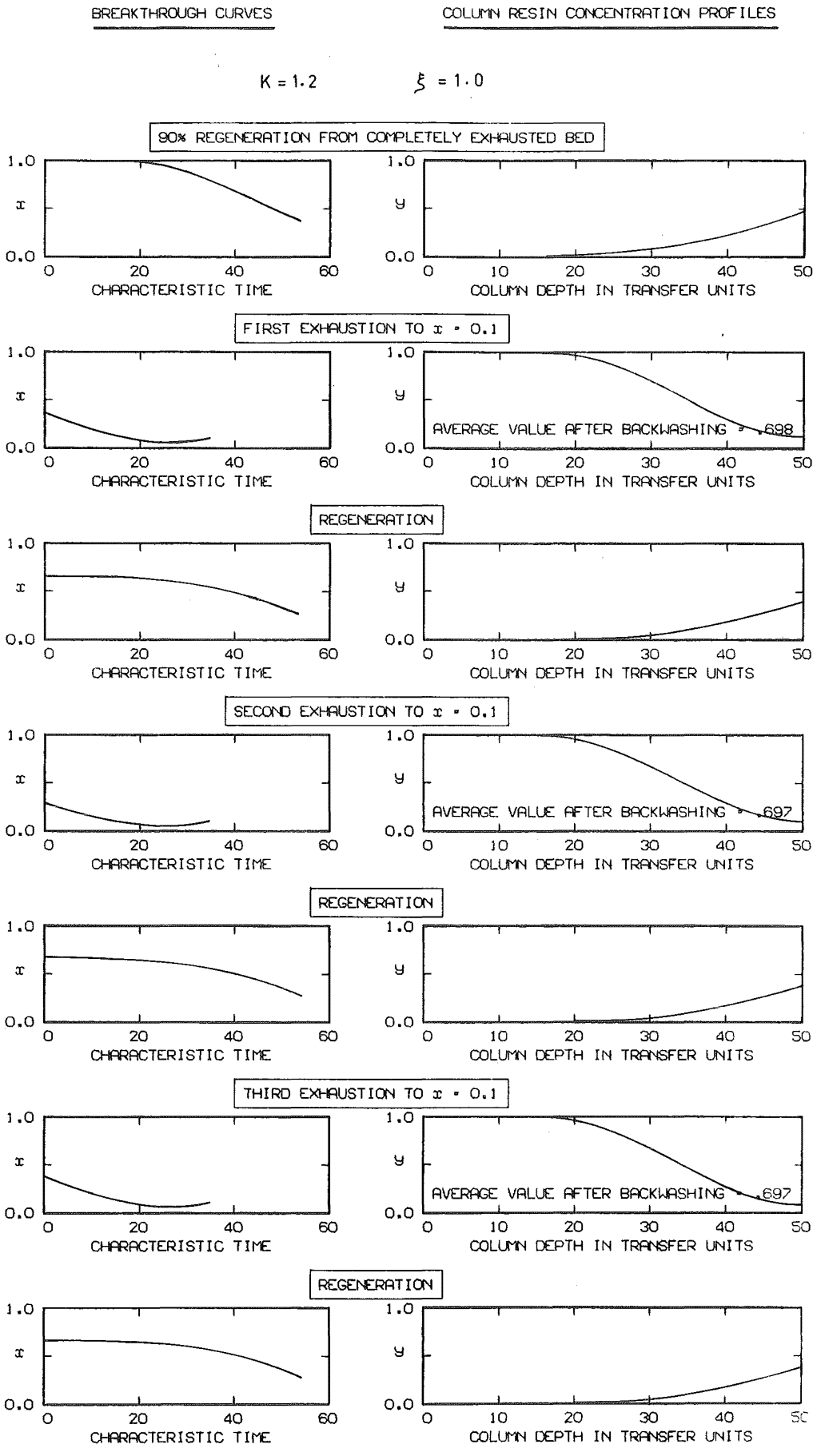
(a) Regeneration of the completely exhausted bed to 90% capacity

(b) A rinse without bed-mixing

(c) Exhaustion to x = 0.1

(d) Back washing with complete bed-mixing

(e) Regeneration again to 90% capacity for three cycles.



GRAPH 10-16. FIXED BED ION EXCHANGE COLUMN SIMULATION FOR CYCLIC OPERATION.

APPENDIX 10A

PROGRAM LISTING - SIXFBC

```
0001        SUBROUTINE SIXFBC(KA,ZET,XO,NDASH,DELN,Y,TDASH,DELT,XDASH)
C
C                SIMULATION OF AN ION EXCHANGE FIXED-BED COLUMN
C
C
C
C    PURPOSE
C
C      THIS SUBROUTINE,GIVEN THE INITIAL COLUMN PRESATURATION RESIN
C    CONCENTRATION PROFILE,Y,AND THE CONCENTRATION HISTORY OF THE FEED,
C    XO,TO THE COLUMN,WILL COMPUTE THE EFFLUENT CONCENTRATION
C    HISTORY AT N=NDASH,AND THE COLUMN RESIN CONCENTRATION
C    PROFILE AT T=TDASH.
C
C    USAGE
C
C      CALL SIXFBC(K,ZETA,XO,NDASH,DELN,Y,TDASH,DELT,XDASH)
C
C    ARGUMENTS
C
C      K       SEPARATION FACTOR
C
C      IF K SET NEGATIVE,THEN THE SEPARATION FACTOR IS ASSUMED TO BE A
C      FUNCTION OF XSTAR.VALUES OF THE SEPARATION FACTOR,EQUALLY SPACED
C      AT XSTAR=0.0(0.05)1.0,MUST BE STORED IN THE COMMON BLOCK KVAL
C
C      ZETA    MECHANISM PARAMETER
C
C      XO      FEED CONCENTRATION VECTOR AT N=0.THERE ARE
C               (TDASH/DELT+1)VALUES REQUIRED AT T=0.0(DELT)TDASH.
C               AS COMPUTATION PROCEDES,XO IS REPLACED BY THE
C               EFFLUENT CONCENTRATION HISTORY AT N=NDASH
C
C      DELT    COMPUTATION STEP-SIZE IN T
C
C      Y       RESIN CONCENTRATION PROFILE AT T=0.0 ON ENTRY TO
C               TO SUBROUTINE.THERE ARE(NDASH/DELN+1)VALUES
C               REQUIRED,SPACED AT N=0.0(DELN)NDASH.AS COMPUTATION
C               PROCEDES,Y IS REPLACED BY THE CONCENTRATION PROFILE
C               AT THE PERTAINING VALUE OF T.
C
C      DELN    COMPUTATION STEP-SIZE IN N
C
C      TDASH   LIMITING VALUE OF T AT CALL,BUT IS REPLACED BY
C              THE PERTAINING VALUE OF T AS COMPUTATION PROCEEDS
C
C      XDASH   THE SIMULATION WILL STOP AND RETURN TO THE
C               CALLING PROGRAM BEFORE T=TDASH IF X.GT.XDASH
C               FOR XDASH POSITIVE,OR IF X.LT.(-XDASH) FOR
```

```
C              XDASH NEGATIVE.
C              TDASH THEN HOLDS THE VALUE OF T.
C
C
C           MIXED DIFFUSION CONTROL  BASIS ON SMALLER NUMBER OF TRANSFER UNITS
C
C
C            BASIS       ZETA      LAMDA        RO         N
C                                  SIGMA        MU
C
C           PARTICLE    LT 1.0      1.0      1.0/ZETA     NP
C
C
C             FILM      GT 1.0      ZETA       1.0        NF
C
C      THE EQUATIONS SOLVED ARE
C           DX/DN+DY/DT=0
C           DY/DT=RATE
C                =LAMDA*(YSTAR-Y)
C                =MU*(X-XSTAR)
C
C
C     SUBPROGRAMS REQUIRED
C
C       RATE     TO LINK TO RATEC OR RATEV AS K IS CONSTANT OR VARIABLE
C       RATEC    RATE FUNCTION,CONSTANT SEPARATION FACTOR,LISTED IN APPENDIX 5B
C       RATEV    RATE FUNCTION,VARIABLE SEPARATION FACTOR,LISTED AS RATE IN
C                  APPENDIX 5D
C
C
0002            REAL X0(1),Y(1)
0003            REAL K,LAMDA,MU,NHI,KA,NDASH
0004            DIMENSION X(1505),R(1505),T(1505)
0005            LOGICAL DEBUG
0006            LOGICAL LINEAR,LIMIT
0007            COMMON ZETA,K,RZETA,RZETAP,FAC1,FAC2,LAMDA,LINEAR,LIMIT,XSTAR,
               1YSTAR
0008            EQUIVALENCE(LAMDA,SIGMA),(RO,MU)
C
C       DEBUG IS TRUE FOR PRINTOUT OF INTERMEDIATE RESULTS
0009            DEBUG=.FALSE.
C                                                                  .EURT.=GUBED
C
C
C     INITIALISATION
C
0010            K=KA
0011            ZETA=ZET
0012            DERT=DELT
```

```
0013              DERN=DELN
0014              NN=NDASH/DELN
0015              NT=TDASH/DELT
0016              NTP1=NT+1
0017              NNP1=NN+1
0018              NNP5=NN+5
                  C
                  C     DECISION ON BASIS
                  C
0019              IF(ZETA.GT.1.00002) GO TO 51
                  C******PARTICLE PHASE BASIS
0020              LAMDA=1.0
0021              GO TO 52
                  C******SOLUTION PHASE BASIS
0022                 51 LAMDA=ZETA
                  C******COMMON VARIABLES FOR RATE FUNCTION
0023                 52 IF(ZETA.GT.1.0E-6)RZETA=1.0/ZETA
0024                 IF(K.LT.0.999.OR.K.GT.1.001) GO TO 56
                  C******LINEAR EQUILIBRIUM
0025              FAC1=1.0
0026              FAC2=1.0
0027              LINEAR=.TRUE.
0028              GO TO 57
                  C******NONLINEAR EQUILIBRIUM
0029                 56 FAC2=ZETA*(K-1.0)
0030              FAC1=(1.0+K*ZETA)/FAC2
0031              FAC2=K/FAC2
0032              LINEAR=.FALSE.
0033                 57 RZETAP=1.0/(ZETA+1.0)
                  C
                  C     SET UP LIMIT
0034              LIMIT=.FALSE.
0035              IF(ZETA.LT.0.001)LIMIT=.TRUE.
                  C
                  C     CALCULATE DOWN IT=1
                  C
0036              XTOP=XO(1)
0037              X(1)=XTOP
0038              R(1)=RATE(X(1),Y(1))
                  C
0039              DO 200 IN=2,NNP1
0040              YD=Y(IN)
0041              X1=X(IN-1)
0042              XD=X1-R(IN-1)*DERN
0043              RD=RATE(XD,YD)
0044              XDD=X1-RD*DERN
0045              X1=(XD+XDD)*0.5
0046              X(IN)=X1
0047              R(IN)=RATE(X1,YD)
```

```
0048            IF(DEBUG.AND.IN.LT.5)WRITE(6,150)IN,XD,YD,RD,XOO,X1,R(IN)
0049          150 FORMAT(1H ,11G12.4)
0050          200 CONTINUE
0051            XO(1)=X(NNP1)
0052            TDASH=0.0
              C
              C     NOW OUTER LOOP FOR INCREASING T
              C
0053            DO 201 IT=2,NTP1
              C
              C     INITIALISE TO TOP OF COLUMN
              C
0054            XTOP=XO(IT)
0055            X(1)=XTOP
0056            Y1=Y(1)
0057            YD=Y1+R(1)*DERT
0058            RD=RATE(XTOP,YD)
0059            YDD=Y1+RD*DERT
0060            Y1=(YD+YDD)/2.0
0061            Y(1)=Y1
              C     INNER LOOP TO STEP DOWN COLUMN
0062            R(1)=RATE(XTOP,Y1)
0063            IF(DEBUG.AND.IT.LT.5)WRITE(6,150)IT,X(1),Y(1),YD,RD,YDD,R(1)
              C
              C
0064            DO 202 IN=2,NNP1
0065            X1=X(IN-1)
0066            Y1=Y(IN-1)
0067            R1=R(IN-1)
0068            X2=X(IN)
0069            Y2=Y(IN)
0070            R2=R(IN)
              C
              C     EVADE CALCULATION IF COLUMN SATURATED
              C
0071            SUMXY=X1+X2+Y1+Y2
0072            IF(SUMXY.GT.3.998.AND.R1.GT.-1.E-10.AND.R2.GT.-1.E-10)GOTO70
              C
              C     EVADE CALCULATION IF COLUMN EMPTY
              C
0073            IF(SUMXY.LT.0.001.AND.R1.LT.1.E-10.AND.R2.LT.1.E-10)GOTO71
              C
              C     FIRST ESTIMATES
              C
0074            XD=X1-DERN*R1
0075            YD=Y2+DERT*R2
0076            RD=RATE(XD,YD)
              C
              C     SECOND ESTIMATES
```

```
C
      XDD=X1-DERN*RD
      YDD=Y2+DERT*RD
C
C     FINAL VALUES
C
      X2=(XD+XDD)/2.0
      Y1=(YD+YDD)/2.0
      R(IN)=RATE(X2,Y1)
      IF(DEBUG.AND.IN.LT.5.AND.IT.LT.5)WRITE(6,150)IN,IT,XD,YD,RD,XDD,
     1YDD,X2,Y1,R(IN)
      IF(ABS(X2-0.5).GT.0.51)CALL DUMP(ZETA,R(NNP1),0)
      X(IN)=X2
      Y(IN)=Y1
  202 CONTINUE
C
C     AT BOTTOM OF COLUMN
C
      XO(IT)=X(NNP1)
      TDASH=(IT-1)*DELT
      IF(DEBUG.AND.IT/5*5.EQ.IT)WRITE(6,157)(X(MM),MM=1,NNP5,1)
  157 FORMAT(1HO,(10G13.5))
C
C     RETURN IF X VALUE AT BOTTOM OF COLUMN HAS
C   RISEN(OR FALLEN)TO SWITCHING VALUE
C
      IF(XDASH.GT.0.0.AND.XO(IT).GE.XDASH.AND.XO(IT-1).LT.XDASH)RETURN
      IF(XDASH.LT.0.0.AND.XO(IT).LE.(-XDASH).AND.XO(IT-1).GT.-(XDASH))
     1RETURN
  201 CONTINUE
      RETURN
C
C     COLUMN SATURATED
   70 X(IN)=1.0
      Y(IN)=1.0
      R(IN)=0.0
      GO TO 202
C
C     COLUMN EMPTY
   71 X(IN)=0.0
      Y(IN)=0.0
      R(IN)=0.0
      GO TO 202
      END
```

```
0001            FUNCTION RATE(X,Y)
                C
                C   PURPOSE
                C
                C     THIS SUBPROGRAM ALLOWS SIXFBC TO USE THE FUNCTION RATEC OR RATEV
                C     AS THE SEPARATION FACTOR IS CONSTANT OR VARIABLE
0002            REAL K
0003            COMMON ZETA,K
0004            IF(K)9,9,10
                C
                C     K VARIABLE
                C
0005          9 RATE=RATEV(X,Y)
0006            RETURN
                C
                C     K CONSTANT
                C
0007         10 RATE=RATEC(X,Y)
0008            RETURN
0009            END
```

CHAPTER 11

CONCLUSIONS

The aim of this thesis was to develop rigorous methods of solving the equations which describe the fixed-bed ion exchange process and thereby to investigate the assumptions and mechanisms significant to column design with the resultant development of short-cut methods for approximate use.

Rigorous models of the fixed-bed ion exchange process have been solved computationally. All have included non-linear equilibrium and distributed mass transfer resistance. Of the more complex models, IXM (or the hybrid equivalent HIXM) has included fickian particle diffusion while HIXL has added terms for axial dispersion. The IXLR model used the simple linear rate expression and produced equivalent results to IXM with less computation and without stability or accuracy problems.

The empirical reaction-kinetic method was used in the form of the computer program VHT to evaluate the analytical expressions involved. Not only does this approach provide the required short-cut method for calculating ion exchange breakthrough curves, by hand if necessary, but its results are so similar to the computed solutions that it should be used in their place for most applications, both for column design and in the analysis of breakthrough behaviour.

The results of IXLR have been successfully compared with experimental data. For those systems for which separate equilibrium measurements had shown that the separation factor varied with solution concentration, this effect must be included in the simulation. In this case, the reaction-kinetic model cannot be used as it assumes a constant separation factor.

Of the other assumptions which lead to analytical solutions (proportionate pattern, constant pattern, linear equilibrium) the linear equilibrium solution is the most mathematically developed, with the BGP program including the effects of distributed mass transfer resistance, a fickian particle rate expression and axial dispersion, but is the least likely to be useful in industrial ion exchange applications. The constant pattern solutions are more likely to be applicable and a

firm guide has been given to the extent of their validity.

The modification of the correlation for N_R in the VHT method to include axial dispersion based on the results of the hybrid computer model HIXL requires further development for very favourable and for very unfavourable equilibrium. For this, the HIXL model (or some digital computer equivalent) should be simplified to use the linear particle rate expression.

The other direction in which this work should continue is towards the investigation of optimum conditions for the fixed bed process in terms of the many design variables available. The reaction-kinetic method, extended to arbitrary initial and boundary conditions, is a sufficiently powerful expression of column behaviour to provide meaningful results, yet simple enough to permit multivariable searching for an optimum without excessive computing time requirements.

NOMENCLATURE

a,b,c	Constants.
A	Column free cross-sectional area (L^2).
b	Correction factor for non-linear equilibrium, Eqn 3-24.
B	Analogue computer time-scale factor, Section 8B-6.
c	Solution concentration, equivalents/litre.
C_o	Total solution concentration, equivalents/litre.
d_p	Particle diameter (L).
D_A, D_B	Self-diffusivity of components A,B in the resin phase (L^2T^{-1}).
D_{AB}	Inter-diffusivity of components A,B in the resin phase (L^2T^{-1}).
D_f	Diffusivity in solution (L^2T^{-1}).
D_p	Particle phase diffusivity (L^2T^{-1}).
D_R	Distribution ratio, $\frac{Q}{\varepsilon C_o}$.
e_A, e_B	Valancies of components A,B.
E_A	Equivalent axial diffusivity (L^2T^{-1}).
F	Solution feed rate to column (L^3T^{-1}).
G	Analogue computer scaling factor, Eqn 8-5.
G1,G2	Analogue computer time-scale factors, Appendix 8B.
h	General finite difference step-size.
I_o	Modified Bessel function of the first kind, of order zero.
J	The J function, Eqn 3-9.
k	Mass transfer coefficient (T^{-1}); k_p, particle phase, Eqn 2-7; k_f, solution phase, Eqn 2-8.
k_R	Reaction rate constant, Eqn 3-20 (T^{-1}).
K	Separation factor, Eqn 2-1.
n_r	Number of radial finite-difference elements used in the particle, Figure 7-2.
N	Dimensionless bed-depth variable, measured in numbers of transfer units, and generally based on the phase with the greater mass transfer resistance; particle phase, $N_p = \frac{Q\, k_p\, z}{C_o\, v}$; solution phase, $N_f = \frac{Q\, k_f\, z}{C_o\, v}$.

N_L Number of axial dispersion transfer units, $\frac{vz}{\varepsilon E_A}$.

N'_p, N'_f Total number of transfer units in the packed bed for the particle, solution phase respectively.

N_{min} The minimum number of transfer units sufficient to provide constant pattern conditions.

N_{pore} Number of transfer units for pore diffusion.

N_R Number of reaction transfer units, Eqns 3-21, 3-24.

N_{Re} Reynolds number.

q Resin concentration, equivalents per volume of packed bed, either bulk value or a function of radial position.

$\bar{q}$ Average resin concentration, equivalents/litre of packed bed.

Q Resin capacity, equivalents/litre of packed column.

r Radial distance (L).

R Fractional radial distance, $\frac{2r}{d_p}$.

R Rate of mass transfer, $\frac{d\bar{y}}{dT}$.

s Dimensionless parameter, $\frac{\sigma \Delta T}{30 (\Delta R)^2}$, Eqns 7-6, 7-7.

S Shifted characteristic time, kt; either particle phase ($S_p = k_p t$) or solution phase basis ($S_f = k_f t$).

t Time, frequently measured from addition of feed solution to the column.

T The characteristic time, either particle phase basis ($T_p = ZN_p$), solution phase basis ($T_f = ZN_f$), or for reaction kinetic solution ($T_R = ZN_R$).

T' The maximum value of the characteristic time for which breakthrough curve values are required.

u Interstitial velocity (LT^{-1}), $\frac{v}{\varepsilon}$.

v Solution superficial velocity (LT^{-1}), $\frac{F}{A}$.

V Effluent volume (L^3).

x Solution concentration ratio, $\frac{c}{c_o}$.

x_o Feed solution concentration ratio.

x^*, y^* Interfacial or equilibrium concentration ratios.

y Resin concentration ratio, $\frac{q}{Q}$, either bulk value or a function of radial position.

$\bar{y}$ Average resin concentration ratio.

z Distance down the packed bed (L).

z' Depth of packing in the column (L).

Z The throughput ratio, $\frac{C_o v}{Qz}\left(t - \frac{\varepsilon z}{v}\right)$.

$\alpha_p, \alpha_f, \alpha_q$ Arbitrary constants in constant pattern equations, Table 3-4 and Eqn 3-18.

α, β, γ Parameters in the Weibull distribution, Eqn 10-5.

$\Delta N, \Delta R, \Delta S, \Delta T$ Step-sizes in N,R,S,T respectively.

ε Packed bed voidage.

θ The dispersion parameter, $\frac{N}{N_L}$.

λ Integration variable, particularly Appendix 9A.

μ Solution viscosity ($ML^{-1}T^{-1}$).

ξ Mechanism parameter, $\frac{N'_p}{N'_f}$

ρ Solution density (ML^{-3})

ρ, σ Parameters in generalised equations, Table 2-1.

ψ A correction factor, Eqn 3-13, for the approximate quadratic rate expression.

LIST OF MODELS AND PROGRAMS

AIXLR	An analogue computer solution of the same equations as IXLR (Chapter 6).
BGP	A digital computer program which is based on the Babcock-Green-Perry equations (Appendix 9A), which includes film and fickian particle diffusion, and axial dispersion, for linear equilibrium only.
GBC	A general tabulation of breakthrough curve values (Appendix 5E) computed using IXLR.
HIXL	An extension of HIXM to include axial dispersion (Chapter 9).
HIXM	A hybrid computer solution of the equations used in IXM (Chapter 8).
IXLR	A model and digital computer program for the fixed-bed ion exchange process, using a linear particle rate expression (Chapter 5).
IXM	Similar to IXLR but including a fickian diffusion expression for particle mass transfer (Chapter 7).
IXVK	A modification of IXLR to allow a variable separation factor (Section 5-7).
SIXFBC	A generalisation of IXLR to arbitrary initial and boundary conditions (Appendix 10A).
VHT	A digital computer program for breakthrough curve calculation using the Vermeulen-Hiester-Thomas method (Appendix 3C) and including correction for axial dispersion (Chapter 9).

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ERRATA

PAGE	LINE	
1-1	10t (from top)	"change" should read "charge"
2-2	8b (from bottom)	"have" should read "has"
2-3	12t	"Helfferich"
2-7	7b	"Donnan"
2-8	7b	"are" should read "is"
2-9	9t	"such" should read "each"
	7b	"Eqn 2-8" should read "Eqn 2-9"
	Eqn 2-10	Each c should be c_i
2-11	Eqn 2-20	$\xi = \frac{N_p'}{\overline{N_f}'}$
2A-2	1b	"dr" should be "dR"
3-1	5b	The right-hand bracket should read $(T_f = ZN_f)$
3-9	8b	"Anzelius"
3-19	10t	"$\overline{R}$" should read "R"
3-22	14b	"intractable"
3-25	Figure 3-6	"The Correction Factor b for Non-linear Equilibrium."
3-28	5b	"particle" should read "partial"
4-3	1t	"particle" should read "partial"
4-5	13b	"Schumann"
4-6	1b, 2b	"Schumann"
	10b	Insert "of" to read "of the same form"
5-2	2t	$\frac{\partial x}{\partial t} + \frac{Q}{\epsilon C_o}\frac{\partial \overline{y}}{\partial t} + \frac{v}{\epsilon}\frac{\partial x}{\partial z} = 0$
Graph 5-14	Heading	0.1 N Ca - Na - Cl
7-14	11b	"requires" should read "requiring"
8-4	2t	"balance"
8-11	3b	"Limit on ΔN"
8-17	16t, 13b	"HIXL" should read "HIXM"

8-21	2b	"Figure 8-7" should read "Figure 8-8"
8-33	11-12b	"providing" should be "provided"
8B-4	16b	Remove "implementation"
9-19	9b	"simultaneously"
9-31	10t	"Eqn 9-19" should read "Eqn 9-18"
10-1	10b	Delete the first occurrence of "mass transfer rate"
10-24	3b	The numerator "$K\left(\frac{N_R}{K}, T_R\right)$" should read "$J\left(\frac{N_R}{K}, T_R\right)$"